PB89-174403

Land Disposal, Remedial Action Incineration and Treatment of Hazardous Waste. Proceedings of the Annual Research Symposium (14th) held at Cincinnati, Ohio, May 9-11, 1988

JACA Corp., Fort Washington, PA

Prepared for

Environmental Protection Agency, Cincinnati, OH

Jul 88

U.S. Department of Commerce
National Technical Information Service
NTIS

United States
Environmental Protection
Agency

Risk Reduction
Engineering Laboratory
Cincinnati OH 45268

EPA/600/9-88/021
July 1988

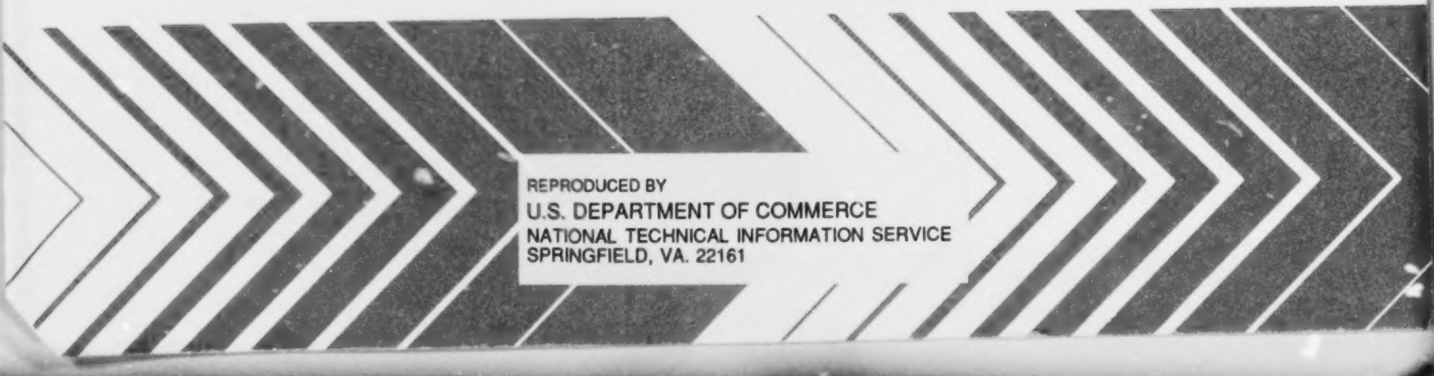
PB89-174403

Research and Development

EPA

Land Disposal, Remedial Action, Incineration and Treatment of Hazardous Waste

Proceedings of the Fourteenth Annual Research Symposium



REPRODUCED BY
U.S. DEPARTMENT OF COMMERCE
NATIONAL TECHNICAL INFORMATION SERVICE
SPRINGFIELD, VA. 22161

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO.
EPA/600/9-88/021

2.

3. RECIPIENT'S ACCESSION NO.
PB89 174403/AS

4. TITLE AND SUBTITLE
Land Disposal, Remedial Action, Incineration
and Treatment of Hazardous Waste

5. REPORT DATE
July, 1988

6. PERFORMING ORGANIZATION CODE

7. AUTHOR(S)

8. PERFORMING ORGANIZATION REPORT NO.

9. PERFORMING ORGANIZATION NAME AND ADDRESS
Coordinated by: JACA Corporation
Fort Washington, PA 19034

10. PROGRAM ELEMENT NO.

11. CONTRACT/GRANT NO.
68-03-3258

12. SPONSORING AGENCY NAME AND ADDRESS
U.S. Environmental Protection Agency
Risk Reduction Engineering Laboratory
Cincinnati, OH 45268

13. TYPE OF REPORT AND PERIOD COVERED
Final:Symposium Proceedings

14. SPONSORING AGENCY CODE
EPA:ORD

15. SUPPLEMENTARY NOTES

16. ABSTRACT

The Fourteenth Annual Research Symposium on Land Disposal, Remedial Action, Incinceration and Treatment of Hazardous Waste was held in Cincinnati, Ohio, May 9-11, 1988. The purpose of this Symposium was to present the latest significant research findings from ongoing and recently completed projects funded by the Risk Reduction Engineering Laboratory (RREL).

These Proceedings are organized in four sections: Session A, Hazardous Waste Land Disposal; Session B, Hazardous Waste Incineration and Treatment; Session A/B, Combined Session; and Session C, RREL Posters. Papers presented by Symposium speakers and abstracts from poster presentations are compiled. Subjects discussed in Session A include remedial action treatment and control technologies for waste disposal, landfill liner and cover systems, personnel protection, underground storage tanks and demonstration and development of innovative/alternative treatment technologies for hazardous waste. Alternative technology subjects include thermal destruction of hazardous wastes, field evaluations, existing treatment options, emerging treatment processes, waste minimization, and biosystems for hazardous waste destruction.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group

18. DISTRIBUTION STATEMENT
Release to Public

19. SECURITY CLASS *(This Report)*
Unclassified

20. SECURITY CLASS *(This page)*
Unclassified

21. NO. OF PAGES
644

22. PRICE

EPA Form 2220-1 (Rev. 4-77) PREVIOUS EDITION IS OBSOLETE

EPA/600/9-88/021
July 1988

LAND DISPOSAL, REMEDIAL ACTION, INCINERATION AND TREATMENT OF HAZARDOUS WASTE

Proceedings of the Fourteenth Annual Research Symposium
at Cincinnati, Ohio, May 9-11, 1988

Sponsored by the U.S. EPA, Office of Research & Development
Risk Reduction Engineering Laboratory
Cincinnati, OH 45268

Coordinated by:

JACA Corp.
Fort Washington, PA 19034

Contract No. 68-03-3258

Project Officers:

John F. Martin
Eugene F. Harris
Cincinnati, OH 45268

RISK REDUCTION ENGINEERING LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
CINCINNATI, OH 45268

NOTICE

These Proceedings have been reviewed in accordance with the U.S. Environmental Protection Agency's peer and administrative review policies and approved for presentation and publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

FOREWORD

Today's rapidly developing and changing technologies and industrial products and practices frequently carry with them the increased generation of materials, that if improperly dealt with, can threaten both public health and the environment. The U.S. Environmental Protection Agency is charged by Congress with protecting the Nation's land, air, and water resources. Under a mandate of national environmental laws, the agency strives to formulate and implement actions leading to a compatible balance between human activities and the ability of natural systems to support and nurture life. These laws direct the EPA to perform research to define our environmental problems, measure the impacts, and search for solutions.

The Risk Reduction Engineering Laboratory is responsible for planning, implementing, and managing research, development, and demonstration programs to provide an authoritative, defensible engineering basis in support of the policies, programs, and regulations of the EPA with respect to drinking water, wastewater, pesticides, toxic substances, solid and hazardous wastes, and Superfund-related activities. This publication is one of the products of that research and provides a vital communication link between the researcher and user community.

These Proceedings from the 1988 Symposium provide the results of projects recently completed by RREL and current information on other projects presently underway. Those wishing additional information on these projects are urged to contact the author or the EPA Project Officer.

RREL sponsors a conference each year in order to assure that the results of its research efforts are rapidly transmitted to the user community. The 1988 conference attracted over 900 attendees from industry, Federal and State agencies, consulting firms and universities. The 1989 conference is planned for April 10, 11, 12 in Cincinnati, OH.

E. Timothy Oppelt, Acting Director
Risk Reduction Engineering Laboratory

ABSTRACT

The Fourteenth Annual Research Symposium on Land Disposal, Remedial Action, Incineration and Treatment of Hazardous Waste was held in Cincinnati, Ohio, May 9-11, 1988. The purpose of this Symposium was to present the latest significant research findings from ongoing and recently completed projects funded by the Hazardous Waste Engineering Research Laboratory (HWERL).

These Proceedings are organized in four sections: Session A, Hazardous Waste Land Disposal; Session B, Hazardous Waste Incineration and Treatment; Session A/B, Combined Session; and Session C, HWERL Posters. Papers presented by Symposium speakers and abstracts from poster presentations are compiled. Subjects discussed in Session A include remedial action treatment and control technologies for waste disposal, landfill liner and cover systems, personnel protection, underground storage tanks and demonstration and development of innovative/alternative treatment technologies for hazardous waste. Alternative technology subjects include thermal destruction of hazardous wastes, field evaluations, existing treatment options, emerging treatment processes, waste minimization, and biosystems for hazardous waste destruction.

CONTENTS

SESSION A - HAZARDOUS WASTE LAND DISPOSAL PAPERS

Page

Technical Resource Documents and Technical Handbooks for Hazardous Wastes Management
Norbert B. Schomaker, U.S. Environmental Protection Agency.......... 1

Underground Storage Tank Corrective Action: Application and Field Evaluation of Vacuum Extraction Technology
William Glynn, Camp Dresser & McKee, Inc............................ 12

Discovery of a New Source of Error in Tightness Tests
Joseph W. Maresca, Jr., Vista Research, Inc......................... 25

Case Histories of Underground Storage Tank Corrective Actions
William M. Kaschak, CDM Federal Programs Corp....................... 39

Dust and Vapor Suppression Technologies for Use During the Excavation of Contaminated Soils, Sludges or Sediments
William Beers, Roy F. Weston, Inc................................. 53

Laboratory Studies of Vacuum-Assisted Steam Stripping of Organic Contaminants from Soil
Arthur E. Lord, Drexel University.................................. 65

Use of Foam Technology for Control of Toxic Gas Releases
Patricia Brown, Enviresponse, Inc.................................. 93

Transport of Inorganic Compounds Through Compacted Clay Soil
David E. Daniel, University of Texas............................... 114

U.S. EPA Research in Solidification/Stabilization of Waste Material
Carlton C. Wiles, U.S. Environmental Protection Agency.............. 126

SITE Demonstration of HAZCON Solidification/Stabilization Process
Paul R. de Percin, U.S. Environmental Protection Agency............. 136

Transport of Dissolved Organics from Dilute Aqueous Solutions Through Flexible Membrane Liners
Henry E. Haxo, Jr., Matrecon, Inc.................................. 145

The Electrical Leak Location Method for Geomembrane Liners
Glenn T. Darilek, Southwest Research Institute...................... 167

Superfund Standard Analytical Reference Matrix Preparation and Results of Physical Soils Washing Experiments
M. Pat Esposito, PEI Associates, Inc............................... 177

Evaluation of Personal Coolers and Vital Signs Monitors for Hazardous Substance Clean-Up Operations
W. Thompson Lawrence, Arthur D. Little, Inc......................... 193

SESSION A (Continued)

Page

Use of Colloidal Gas Aphrons for In-Situ Biodegradation of Contaminated Ground Water
Donald L. Michelsen, Virginia Polytechnic Institute.................. 203

Expert Systems to Assist in Review of Closure Plans for Land Disposal Sites
Daniel G. Greathouse, U.S. Environmental Protection Agency.......... 218

Development of a Novel Support Aerated Biofilm Reactor for the Biodegradation of Toxic Organic Compounds
Kenneth Williamson, Oregon State University......................... 225

Microbial Mineralization of Organic Contaminants on Soils and Soil Fractions
D.S. Kosson, Rutgers, The State University of New Jersey............ 237

Biological Treatment of Leachate/New Lyme, Ohio
Edward J. Opatken, U.S. Environmental Protection Agency............. 247

SESSION B - HAZARDOUS WASTE INCINERATION AND TREATMENT PAPERS

Page

Trial Burn Reporting and Development of Permit Conditions
Sonya M. Stelmack, U.S. Environmental Protection Agency............. 258

Rotary Kiln Incineration: The Effect of Oxygen Enrichment on Formation of Transient Puff During Batch Introduction of Hazardous Wastes
William P. Linak, U.S. Environmental Protection Agency.............. 270

Pathways of PIC Formation in Hazardous Waste Incinerators
B. Dellinger, University of Dayton Research Institute............... 289

Studies of POHC DE During Simulated Atomization Failure in a Turbulent Flame Reactor
Daniel P.Y. Chang, University of California, Davis.................. 301

Review of Research Testing Activities at the U.S. EPA Combustion Research Facility
Robert E. Mournighan, U.S. Environmental Protection Agency.......... 317

Pilot-Scale Boiler Cofiring Tests to Investigate Nonsteady Effects
H.B. Mason, Acurex Corporation....................................... 332

Oxidation of Polychlorinated Biphenyls by Pseudomonas putida LB400
Sadhana Singh, The University of Texas at Austin.................... 346

Biological Oxidations of Organic Compounds by Enzymes from a White Rot Fungus
J.A. Bumpus, Utah State University.................................. 355

Detoxification of Contaminated Sludges Using Combined Microbiological and Photolytic Degradative Approaches
Ralph J. Portier, Louisiana State University......................... 371

Testing of Treatment Systems for Cyanide Bearing Hazardous Wastes
Sardar Q. Hassan, University of Cincinnati.......................... 390

Field Experience with the KPEG Reagent
Alfred Kornel, U.S. Environmental Protection Agency................. 403

Demetallation of Used Oil to Facilitate Use as a Non-Hazardous Fuel
Ray Tarrer, Auburn University.. 414

The Incomplete Combustion of Carbon Tetrachloride During Normal/Abnormal Hazardous Waste Incineration
Robert C. Thurnau, U.S. Environmental Protection Agency............. 444

Hazardous Waste Incineration Prior to Land Disposal
Ronald Turner, U.S. Environmental Protection Agency................. 456

SESSION B (Continued)

Page

Assessment of Volatile Organic Air Emissions from an Industrial Aerated Wastewater Treatment Tank
Bart Eklund, Radian Corporation.................................... 468

California Department of Health Services/EPA Status Update of the California Land Disposal Restrictions and Impact/Implementation Program
Robert Ludwig, California Department of Health Services............. 476

The EPA Manual for Waste Minimization Opportunity Assessments
Michael Meltzer, Jacobs Engineering Group.......................... 486

Case Studies of Waste Minimization Assessments for Cyanide Wastes from Electroplating Operations
Deborah Hanlon, Jacobs Engineering Group............................ 495

SESSION A/B - COMBINED SESSION

Page

TCLP As A Means of Treatment Effectiveness: Results of TCLP Work Completed on Different Treatment Technologies for CERCLA Soils
Robert C. Thurnau, U.S. Environmental Protection Agency............. 509

Application of Low-Temperature Thermal Treatment Technology to CERCLA Soils
Michael F. Szabo, PEI Associates, Inc................................ 529

Evaluation of Solidification/Stabilization as a Best Demonstrated Available Technology
Leo Weitzman, Acurex Corporation..................................... 542

SITE Demonstration of the Shirco Infrared Incinerator
Howard O. Wall, U.S. Environmental Protection Agency................ 558

Demonstration of the Pyretron™ Enhanced Oxygen Burner at the U.S. EPA Combustion Research Facility
Laurel Staley, U.S. Environmental Protection Agency................. 571

Terra Vac In-Situ Vacuum Extraction Process SITE Demonstration
Mary K. Stinson, U.S. Environmental Protection Agency............... 591

SESSION C - HWERL POSTER PRESENTATIONS

Page

White Rot Fungus Development Program
John A. Glaser, U.S. Environmental Protection Agency................ 604

The Impact of a Model Organic Leachate on Slurry Wall Performance
Richard M. McCandless, University of Cincinnati..................... 605

Biological Treatment of Aqueous Organic Hazardous Waste
Lisa M. Brown, U.S. Environmental Protection Agency................. 607

Decontamination of Buildings, Equipment and Debris at Superfund Sites
Michael L. Taylor, PEI Associates, Inc.............................. 608

Characterization of 2,4,5-T Degradative Genes in *Pseudomonas cepacia* Strain AC1100 and Spontaneous Mutants
R.A. Haugland, University of Illinois at Chicago.................... 610

Demonstrate Computer Assisted Engineering (CAE) Techniques for Remedial Action Assessment
P.R. Cluxton, University of Cincinnati.............................. 611

Activities of the Louisiana State University Hazardous Waste Research Center
Danny D. Reible, Louisiana State University......................... 612

Innovative Delivery and Recovery Systems: Hydraulic Fracturing
Larry Murdoch, University of Cincinnati............................. 613

Incineration of Nitrated Pesticides in a Low NOx Precombustor/Package Boiler Simulator
William P. Linak, U.S. Environmental Protection Agency.............. 614

Assessment of International Technologies for Superfund Applications
Thomas J. Nunno, Alliance Technologies.............................. 615

Prediction of the Fate of Toxic Metals in Hazardous Waste Incinerators
R.G. Barton, Energy and Environmental Research Corporation.......... 616

Loading Point Puncturability Analysis of Geosynthetic Liner Materials
Daren L. Laine, Southwest Research Institute........................ 618

Results of a Laboratory Characterization of Pulp and Paper Mill Sludge and Fly Ash for Potential Utilization as Hydraulic Barrier Construction Materials in Landfills
Van Maltby, Natonal Council for the Paper Industry for Air and Stream Improvement, Inc... 620

The U.S. EPA Combustion Research Facility
Larry R. Waterland, Acurex Corporation.............................. 621

SESSION C (Continued)

Page

The Waste Reduction Innovative Technology Evaluation (WRITE) Program
Mike Szabo, PEI Associates, Inc. 622

Case Histories of Underground Storage Tank Corrective Actions
Joyce K. Hargrove, CDM Federal Programs Corporation 623

Hospital Waste Incineration
Teri L. Shearer, U.S. Environmental Protection Agency 624

Assessment of Solidification/Stabilization Technologies for Superfund Contaminated Soils
Richard M. McCandless, University of Cincinnati 625

Small Quantity Generator Research Program: Minnesota Technical Assistance Program
Cindy A. McComas, University of Minnesota 626

Pilot-Scale Physical Separations for Treatment of Organic Hazardous Wastes
Jeffrey P. Herrin, University of Cincinnati 627

Applications of Supercritical Extraction to Environmental Control
Gregory W. Leman, University of Illinois 628

Results of a Trial Burn of EPA's Mobile Incineration System
Gopal Gupta, Enviresponse, Inc 629

TECHNICAL RESOURCE DOCUMENTS AND TECHNICAL HANDBOOKS FOR HAZARDOUS WASTES MANAGEMENT

Norbert B. Schomaker
and
Daniel W. Farrell
U.S. Environmental Protection Agency
Cincinnati, Ohio 45268

ABSTRACT

The Environmental Protection Agency is developing and updating a series of Technical Resource Documents (TRD's) and Technical Handbooks to provide best engineering control technology to meet the needs of the Resource Conservation and Recovery Act (RCRA) and the Comprehensive Environmental Response Compensation and Liability Act (CERCLA) respectively. These documents and handbooks are the compilation of the Land Pollution Control Division's (LPCD) research efforts to date. The specific areas of research being conducted under the RCRA land disposal program relate to laboratory, pilot and field validation studies in cover systems, waste leaching and solidification, liner systems and disposal facility evaluation. The specific areas of research being conducted under the CERCLA uncontrolled waste sites (Superfund) program relate to pilot and field validation studies in barriers, waste storage, waste treatment, modeling and post-closure evaluation. The Technical Resource Documents are intended to assist both the regulated community and the permitting authorities, as well as support the RCRA Technical Guidance Documents prepared by EPA's Office of Solid Waste (OSW). The Technical Handbooks provide the EPA Program Offices and Regions, as well as the states and other interested parties, with the latest information relevant to remedial actions.

INTRODUCTION

Land disposal of hazardous waste is subject to requirements in Subtitle C of the Resource Conservation and Recovery Act (RCRA) of 1976 and in the 1984 Amendments to this Act, requiring that treatment, storage or disposal of hazardous waste be carried out in accordance with the RCRA regulations. Owners and operators of new facilities must apply for and receive a RCRA permit before beginning operation of such a facility.

The clean up or containment technology associated with remedial action at an existing uncontrolled hazardous waste site is subject to the requirements of the Comprehensive Environmental Response, Compensation, and Liability Act of 1980 (CERCLA or Superfund) and the Superfund Amendments and Reauthorization Act of 1986 (SARA) which require the evaluation of remedial action clean up technologies.

To meet the Control Technology aspects of RCRA and CERCLA as related to Land Disposal Facilities, the research program has relied heavily upon the containment aspects of the wastes at the facility or site. The containment aspects of waste disposal onto the land need to address the development of performance and operational standards for new waste disposal facilities (RCRA sites) and the containment or destruction of pollutants emanating from existing waste disposal facilities (CERCLA sites). The control technology research approach being pursued by the USEPA is to develop an improved data base so that current waste disposal practices can be upgraded by developing proper site selection criteria and control technology for the establishment of new waste disposal facilities, and to develop improved containment technology for existing waste disposal sites by minimizing pollutant generation and release to the environment.

The development of proper control technology for new (RCRA) waste disposal facilities will combine information from laboratory, pilot and field validation studies in the research areas of cover systems, waste leaching, solidification, liner systems, and disposal facility evaluation. Cover systems research is developing and evaluating the effectiveness of various material components (i.e., vegetation, soils, membranes, and drainage blankets) in relation to the cover function of minimizing moisture ingress and gas egress. Waste leaching research is investigating techniques for predicting the composition of actual field leachates from samples of wastes or mixtures of wastes. Waste solidification research is evaluating the effectiveness and performance with time of chemical stabilization and encapsulation processes to minimize the release of leachate and gas pollutants to the environment. Disposal facility evaluation research is evaluating effective techniques to ensure that land disposal facilities are built as designed for either permanent disposal or short/long term storage. Incorporated throughout the research for development of control technology for new waste disposal facilities is a continuous technology transfer and assistance program of activity for the program office and regional offices and user communities. The Technical Resource Documents (TRD's) are considered to be primary documents for transferring current RCRA control technologies to the user. The TRD's are being developed and published to assist the permit applicants and permit review officials to assure that the latest containment facility technology is being utilized. The TRD's are to be used in conjunction with the Technical Guidance Documents being prepared by OSW. The documents contain guidance, not regulations or requirements, which the Agency believes comply with Design and Operating Requirements contained in Part 264 of the regulations. The information and guidance presented in these documents constitute a suggested approach for review and evaluation based on good engineering practices. There may be alternative and equivalent methods for conducting the review and evaluation. However, if the results of these methods differ from those of the Environmental Protection Agency's method, they may have to be validated by the applicant.

The development of proper containment technology to upgrade existing (CERCLA) waste disposal facilities will combine information from the above described program for new waste disposal facilities along with pilot and field validation studies in the research areas of barriers, waste storage, waste treatment, modeling, and post-closure evaluation. Barrier research is developing and evaluating in-situ control technologies to contain or minimize pollutant releases from uncontrolled sites and to predict performance with time. In-situ control technologies such as slurry walls, grout curtains, cutoff walls, and covers are being evaluated. Waste storage research is evaluating the cost effectiveness of placing wastes from the clean up of uncontrolled sites into mines or above ground storage facilities. Also, packaging of hazardous wastes in various containers is being investigated. Waste treatment research is evaluating the effectiveness of various techniques for transferring the wastes or collected leachates in-place or on-site. Techniques such as stabilization, encapsulation, permeable treatment walls, microbial degradation, and physical/chemical treatment are being investigated. Modeling technology has been developed for evaluation of remedial action alternatives and will be updated to reflect improved performance, reliability, and cost information from field scale studies, case studies and other research areas. Post-closure research is evaluating the criteria for final site usage once the disposal facility has been remediated. Incorporated throughout the research on development of control technology for existing waste disposal facilities is a continuous technology transfer and assistance program of activity for the program office and user communities. The Technical Handbooks are considered to be the primary documents for transferring current CERCLA containment technology to the user.

TECHNICAL RESOURCE DOCUMENTS

Seven TRD's have been completed to date. Five of the TRD's are related to landfills, and one document each is related to surface impoundments and land treatment. A listing of these documents is shown below, along with a brief description, publication number, and the project officer's name in parentheses. (See Table 1 for a summarized price list.)

Evaluating Cover Systems for Solid and Hazardous Waste (SW-867)

A critical part of the sequence of designing, constructing, and maintaining an effective cover over solid and hazardous waste sites is the evaluation of engineering plans. All aspects of covers are addressed in detail to allow for a complete evaluation of the entire cover system. There are eleven sequential procedures identified for evaluating engineering plans.

The document describes current technology for landfill covers in three broad areas: data examination, evaluation steps and post-closure plan. Data examination discusses test data review procedure, topographical data review and climatological data review procedures. The evaluation steps include placement, vegetation, drainage, cover composition, thickness and configuration. The post-closure aspects include maintenance and contingency plan evaluation procedures. There are 36 specific steps regarding the preceding factors which are recommended to be followed in evaluating a permit for a cover for hazardous waste. PB 87-154894 (R.E. Landreth)

Landfill and Surface Impoundment Performance Evaluation (SW-869)

The evaluation of leachate collection systems using compacted clay or synthetic liners to determine how much leachate will be collected and how much will seep through the liner into underlying soils is presented. The adequacy of sand and gravel drain layers, slope, and pipe spacing is also covered. The author has allowed for the widely varied technical backgrounds of his intended audience by presenting, in full, the rigorous mathematics involved in reaching his final equations. Thus, any evaluator can take full advantage of the manual up to the level of his own mathematical proficiency. PB 81-166357 (M.H. Roulier)

Lining of Waste Impoundment and Disposal Facilities (SW-870)

This document provides information on performance, selection, and installation of geosynthetics, including flexible membrane liners, geonets, geotextiles, and other natural drainage media, for specific disposal situations, based upon the current state-of-the-art of liner technology and other pertinent technologies. It contains descriptions of wastes and their effects on linings, a full description of various natural and artificial liners, service life and failure mechanisms, installation problems and requirements of liner types, costs of liners and installation, and tests that are necessary for pre-installation and monitoring surveys. A revised version should be available in late 1988. PB 86-192796 (R.E. Landreth)

Management of Hazardous Waste Leachate (SW-871)

This document has been prepared to provide guidance for permit officials and disposal site operators on available management options for controlling, treating, and disposing of hazardous waste leachates. It discusses considerations necessary to develop sound management plans for leachate generated at surface impoundments and landfills. Management may take the form of leachate collection and treatment or pretreatment of the wastes. PB 81-189359 (S.C. James)

Guide to the Disposal of Chemically Stabilized and Solidified Wastes (SW-872)

The purpose of this TRD is to provide guidance in the use of chemical stabilization/solidification techniques for limiting hazards posed by toxic wastes in the environment, and to assist in the evaluation of permit applications related to this disposal technology. The document addresses the treatment of hazardous waste for disposal or long term storage and surveys the current state and effectiveness of waste treatment technology. A summary of the major physical and chemical properties of treated wastes is presented. A listing of major suppliers of stabilization and solidification technology and a summary of each process is included. PB 87-154902 (R.E. Landreth)

Closure of Hazardous Waste Surface Impoundments (SW-873)

The methods, tests, and procedures involved in closing a surface impoundment are discussed and referenced. Problems related to now abandoned methods, such as waste removal or consolidating the waste on-site and securing the site as a landfill, are also discussed. It is written primarily for staff members in EPA regional offices or state regulatory offices, who are charged with evaluating and approving closure plans for surface impoundments under regulations of the Resource Conservation and Recovery Act of 1976. Methods of assessing site closure considerations are documented. PB 87-155537 (M.H. Roulier)

Hazardous Waste Land Treatment (SW-874)

The objectives of "Hazardous Waste Land Treatment" are to describe current technology and to provide methods for evaluating the performance of an applicant's hazardous waste land treatment facility design. Land treatment is approached comprehensively from initial site selection through final closure, and additional information sources are referenced liberally. Land treatment, which involves using the surface soil as the treatment medium, is already widely practiced by some industries for handling their hazardous wastes. PB 81-182107 (C.C. Wiles)

FUTURE TECHNICAL RESOURCE DOCUMENTS

Additional TRD's now being developed or in planning stages by the Office of Research and Development are included here for reference. A listing of these documents is shown below, along with a brief description and the project officer's name in parentheses.

Solid Waste Leaching Procedures Manual (SW-924)

This is a report on laboratory batch procedures for extracting or leaching a sample of solid waste so that the composition of the lab leachate is similar to the composition of leachate from waste under field conditions. This TRD was originally published by OSW in March 1984 for public comment and has subsequently been revised. This draft document will not be published as is because of possible confusion with other leaching tests such as the EP and TCLP. Some of the data in this TRD will be incorporated into a document on monofill leaching. PB 87-152054 (C.I. Mashni)

Soil Properties, Classification, and Hydraulic Conductivity Testing (DRAFT) (SW-925)

This report is a compilation of available laboratory and field testing methods for the measurement of hydraulic conductivity (permeability) of soils. Background information on soil classification, soil water, and soil compaction are included along with descriptions of sixteen methods for determination of saturated or unsaturated hydraulic conductivity. This TRD has been revised to incorporate public comments and is presently at OSW where it will be published in the near future. PB 87-155784 (M.H. Roulier)

Batch Type Adsorption Procedures for Estimating Soil Attenuation of Chemicals

This TRD summarizes laboratory batch procedures for assessing the capacity of soils to attenuate chemical constituents from solutions such as leachates. It explains the scientific basis and rationale for these procedures and the use of data in designing soil liners for pollutant retention. It was issued for public comment in May 1987 and is intended for revision in late 1988. PB 87-146155 (M.H. Roulier)

Methods for the Prediction of Leachate Plume Migration and Mixing

This project evaluated a variety of computer programs for hand-held calculators, micro- and macro-computers but because of other priorities it has been effectively cancelled as of March 1988. (M.H. Roulier)

Hydrologic Evaluation of Landfill Performance (HELP) Model

The HELP Model is a modification of the original waste disposal site hydrologic model entitled, "Hydrologic Simulation on Solid Waste Disposal Sites." This update has incorporated the two-dimensional aspects of landfill cover leachate collection system. OSW published this TRD (SW-84-009 and SW-84-010) for public comment in two volumes. These two volumes are available from NTIS and include the user's guide for Version 1 and documentation and description of the program. The HELP Model (Version 1) is also available for the IBM PC/XT or compatible computers. Version 2 of the HELP Model is being developed to incorporate public comments and results from verification studies and will be published in late 1988. PB 85-100840 and PB 85-100832 (R.E. Landreth)

Design, Construction, Maintenance, and Evaluation of Clay Liners for Hazardous Waste Facilities

This 600-page TRD summarizes the state-of-the-art for clay liners as of August 1985. It was issued for public comment in December 1986, has subsequently been revised, and will be published in late 1988. PB 86-184496 (M.H. Roulier)

TECHNICAL HANDBOOKS

Eleven technical handbooks have been completed to date. These handbooks cover a variety of techniques on general remedial action guidance, in-place treatment, barriers, decontamination and modeling. A listing of those documents which contain unique state-of-the-art information is shown below, along with a brief description, publication number, and the project officer's name in parentheses. (See Table 2 for a summarized price list.)

Review of In-Place Treatment Techniques for Contaminated Surface Soils

This two-volume report presents information on in-place treatment technologies applicable to contaminated soils less than 2 feet in depth. Volume 1 discusses the selection of the appropriate in-place treatment technology. Volume 2 provides background information and relevant chemical data. Selection of in-place treatment technologies follows the process outlined in the National Contingency Plan. The type of in-place treatment (extraction, immobilization, degradation, attenuation, or reduction of volatiles) is determined on the basis of information available from the remedial investigation. Selection of a specific technology involves assessment of waste, soil, and site-specific variables. The technology is implemented if it is considered more cost-effective in comparison with the other alternatives. Volume 1: Technical Evaluation, PB 85-124881 and Volume 2: Background Information, PB 85-124899 (N.P. Barkley)

Handbook: Remedial Action at Waste Disposal Sites (REVISED)

The objectives of the Handbook are twofold: (1) to provide the reader with a generalized understanding of the pollutant pathways involved in waste disposal sites, the remedial actions as they apply to each pathway, and the process of selecting the appropriate remedial actions; and (2) to provide detailed information on specific remedial actions including applications, state-of-the-art, design, construction, and/or operating considerations, advantages, disadvantages and cost.
PB 87-201034 (D.E. Sanning)

Handbook for Evaluating Remedial Action Technology Plans

This Remedial Action Technical Resource Document describes how the technologies and methods for evaluating proposed new RCRA hazardous waste disposal sites can be applied to site-specific remedial response activities for uncontrolled hazardous waste sites. The Remedial Action Document is based on the state-of-the-art technical and cost information in seven TRD's for design and evaluation of new hazardous waste disposal sites, and then edited to address the needs of personnel involved in response and remedial action planning under CERCLA. PB 84-118249 (H.R. Pahren)

Slurry Trench Construction for Pollution Migration Control

A guidance manual for slurry trench cutoff wall design, construction, and performance evaluation provides recommendations on a variety of scientific and technical parameters relevant to using this approach to isolate hazardous chemicals in near-surface groundwater regimes. The accomplishment of this effort required extensive information gathering and integration of technical data gathered from a diverse array of experience and authorities.
PB 84-177831 (W.E. Grube)

Guide for Decontaminating Buildings, Structures and Equipment at Superfund Sites

A decontamination manual was designed for EPA Program Offices and Regional Superfund Programs as part of the restoration profile of Superfund sites. The manual gives guidelines on 1) the extent to which contamination of buildings, structures and construction equipment can be reduced or eliminated, 2) decontamination methods, 3) economics, 4) health hazards, and 5) availability of equipment/personnel for the detoxification procedures. Specific waste types found in contaminated buildings, structures and equipment at Superfund sites are identified. Potential secondary impacts of available and potential decontamination treatment methods are addressed in this study. Costs versus risk and projected ultimate site usage are addressed. Methods for monitoring the successfulness of various procedures are defined. PB 85-201234 (N.P. Barkley)

Modeling Remedial Actions at Uncontrolled Hazardous Waste Sites

The objective of this document is to provide technical guidance on the selection and application of models for evaluating remedial action alternatives at uncontrolled hazardous waste sites. The volumes cover selection of models, simplified methods for subsurface and waste control actions, numerical modeling of surface, subsurface and waste control actions, and analytical and numerical models for evaluation of surface water remedial actions. PB 85-211357 (R.E. Landreth)

Leachate Plume Management

This Handbook summarizes information of leachate plume dynamics and plume management alternatives gained by a study of leachate plume management techniques. Factors that affect leachate plume movement, key considerations in delineating the current and future extent of the leachate plume, technologies for controlling the migration of plumes, and criteria for evaluating and selecting plume management alternatives are discussed. PB 86-122330 (N.P. Barkley)

Systems to Accelerate In-Situ Stabilization of Waste Deposits

This document investigates in-situ systems which accelerate the stabilization of waste deposits. In-situ applications involve three essential elements: selection of chemical or biological agent (reactant) which can react with and stabilize the waste, a method for delivery of the reactant to the deposit and a method for recovery of the reaction products or mobilized waste. Four reactant categories have been examined: biodegradation, surfactant assistant flushing, hydrolysis, and oxidation. Methods of delivery of reactants based upon gravity include surface flooding, ponding, surface spraying, ditching, and infiltration beds and galleries. Forced injection (pumping) may also be used. Recovery systems using gravity include open ditching and buried drains, and pumped methods include well-point and deep well systems. PB 87-112306 (W.E. Grube)

Covers for Uncontrolled Hazardous Waste Sites

A handbook has been developed which can be used as a guidance document for the selection, design, installation, and long-term maintenance of covers as remedial actions. This handbook provides technical information for regulatory personnel as well as guidance for cover-system designers and construction engineers. PB 87-119483 (J.M. Houthoofd)

Handbook for Stabilization/Solidification of Hazardous Waste

Another handbook has been developed to provide guidance for the evaluation, selection, and use of solidification/ stabilization technology as a remedial action alternative at uncontrolled hazardous waste sites. The planning for the application of solidification/ stabilization is divided into two phases: process selection and scenario selection. Process selection is concerned with the chemistry of the stabilization/ solidification processes in the identification of the composition of the waste. Presented in the handbook are testing and analysis techniques for characterizing waste as a basis for selection of pretreatment and stabilization/solidification processes. Also data are developed on the compatibility of additives and specific classes of waste; and testing systems for the evaluation of stabilized/solidified wastes are reviewed. Scenario selection is concerned with the development of equipment requirements, construction sequencing, and cost estimating for the chosen solidification/stabilization process. The handbook presents four basic field scenarios, based on field surveys, that have been used successfully. PB 87-116745 (J.M. Houthoofd)

Handbook: Dust Control at Hazardous Waste Sites

Field studies were performed to determine the effectiveness of dust control technologies at hazardous sites. In the first field study, dust suppressants were tested to determine the effectiveness of fugitive dust control against wind erosion from exposed areas. Based on a tracer sampling protocol, the suppressants were 100 percent effective for 1 to 4 weeks after application, with declining control efficiencies thereafter. The second field study was an evaluation of the effectiveness of windscreens and windscreen/dust suppressant combinations in controlling fugitive dust from storage piles. PB 86-190105 (S.C. James)

CONCLUSION

The Technical Resource Documents and the Technical Handbooks that are being prepared and updated by the Land Pollution Control Division (LPCD) are a series of documents which provide best engineering control technology to meet the needs of RCRA and CERCLA, respectively. The TRD's provide design, operation, and evaluation information related to new RCRA hazardous waste disposal facilities to assist the regulated community and the permitting authorities. The Technical Handbooks provide reliable and cost effective remedial action technology information related to Superfund facilities to assist the user community and on-scene coordinators. These documents and handbooks present the sum total of the body of information and experience gained by the EPA over the years on a given topic. As new information is developed, the Agency intends to update each of these documents and handbooks so that they reflect the latest state-of-the-art information.

More information about a specific project or study can be obtained by contacting the project officer referred to in the text. Project Officers can be contacted by writing or telephoning the USEPA, Hazardous Waste Engineering Research Laboratory, Land Pollution Control Division, 26 West Martin Luther King Drive, Cincinnati, Ohio 45268. Phone: (513) 569-7871

TABLE 1. Technical Resource Documents

		NTIS No.	Price List*
SW-867	Evaluating Cover Systems for Solid and Hazardous Waste	PB 87-154-894	$14.95
SW-869	Landfill and Surface Impoundment Performance Evaluation	PB 81-166-357	$14.95
SW-870	Lining of Waste Impoundment and Disposal Facilities	PB 86-192-796	$38.95
SW-871	Management of Hazardous Waste Leachate	PB 81-189-359	$19.95
SW-872	Guide to the Disposal of Chemically Stabilized and Solidified Wastes	PB 87-154-902	$14.95
SW-873	Closure of Hazardous Waste Surface Impoundments	PB 87-155-537	$19.95
SW-874	Hazardous Waste Land Treatment	PB 81-182-107	$68.95
SW-924	Solid Waste Leaching Procedures Manual	PB 87-152-054	$19.95
SW-925	Soil Properties, Classification, and Hydraulic Conductivity Testing (DRAFT)	PB 87-155-784	$19.95
	Batch Type Adsorption Procedures for Estimating Soil Attenuation of Chemicals	PB 87-146-155	$19.95
	Methods for the Prediction of Leachate Plume Migration and Mixing	N/A	N/A
	Hydrologic Evaluation of Landfill Performance (HELP) Model: Volume 1	PB 85-100-840	$19.95
	Hydrologic Evaluation of Landfill Performance (HELP) Model: Volume 2	PB 85-100-832	$25.95
	Design, Construction, Maintenance, and Evaluation of Clay Liners for Hazardous Waste Facilities	PB 86-184-496	$44.95

* Documents can be purchased from NTIS by requesting the stock number
Prices are effective through 1988.
Add $3.00 for shipping/handling charge per order.

National Technical Information Service
5285 Port Royal Road
Springfield, VA 22161
Telephone: (703) 487-4650
(FTS) 737-4600

TABLE 2. Technical Handbooks

	NTIS No.	Price List*
Review of In-Place Treatment Techniques for Contaminated Surface Soils: Volume 1	PB 85-124-881	$19.95
Review of In-Place Treatment Techniques for Contaminated Surface Soils: Volume 2	PB 85-124-899	$32.95
Handbook: Remedial Action at Waste Disposal Sites (REVISED)	PB 87-201-034	$50.95
Handbook for Evaluating Remedial Action Technology Plans	PB 84-118-249	$38.95
Slurry Trench Construction for Pollution Migration Control	PB 84-177-831	$25.95
Guide for Decontaminating Buildings, Structures and Equipment at Superfund Sites	PB 85-201-234	$25.95
Modeling Remedial Actions at Uncontrolled Hazarous Waste Sites	PB 85-211-357	$38.95
Leachate Plume Management	PB 86-122-330	$50.95
Systems to Accelerate In-situ Stabilization of Waste Deposits	PB 87-112-306	$32.95
Covers for Uncontrolled Hazardous Waste Sites	PB 87-119-483	$44.95
Handbook for Stabilization/Solidification of Hazardous Waste	PB 87-116-745	$19.95
Handbook: Dust Control at Hazardous Waste Sites	PB 86-190-105	$14.95

* Documents can be purchased from NTIS by requesting the stock number.
Prices are effective through 1988.
Add $3.00 for shipping/handling charge per order.

National Technical Information Service
5285 Port Royal Road
Springfield, VA 22161
Telephone: (703) 487-4650
(FTS) 737-4600

UNDERGROUND STORAGE TANK CORRECTIVE ACTION: APPLICATION AND FIELD EVALUATION OF VACUUM EXTRACTION TECHNOLOGY

William Glynn
Camp Dresser & McKee Inc.
Boston, MA 02108

Chi-Yuan Fan
U.S. Environmental Protection Agency
Hazardous Waste Engineering Research Laboratory
Release Controls Branch
Edison, New Jersey 08837

ABSTRACT

The problems associated with leakage of motor fuels from underground storage tanks (USTs) are compounded by a general lack of understanding of the effectiveness of corrective actions toward the cleanup of hydrocarbons in the subsurface environment. The application of vacuum extraction technology to the cleanup of released volatile organics in the soil environment requires an understanding of the subsurface environmental conditions and the removal mechanisms. The effectiveness and/or limitations of vacuum extraction technology as applied to a gasoline station site in Belleview, Florida is evaluated. This paper presents a preliminary assessment of the vacuum extraction system, as the study was conducted at the end of the cleanup program at the Belleview site.

Benzene (B), toluene (T), ethylbenzene (E), xylenes (X), and other volatile gasoline components were continuously removed from the subsurface zones by application of a vacuum extraction system. During the 25-day EPA evaluation of the Belleview, Florida site, where the initial soil concentrations of total BTEX ranged from 1.0 to 10 ug/g, a total of 10 kilograms of BTEX and 90 kilograms of total hydrocarbons, as BTEX equivalent, were removed. The quantity of contaminants withdrawn from each extraction well varied greatly over the spatial distribution of the site and the soil type with the same applied vacuum.

INTRODUCTION

Approximately three to five million underground storage tanks in the United States are used to store liquid petroleum and chemical substances. Further, estimates indicate that 100,000 to 400,000 of these tanks and their associated piping systems may be - or have been - leaking. A large fraction of these leaks have been of gasoline and other petroleum distillates. The resulting contamination of the environment, especially of groundwater used for water supply, has left the United States with a massive cleanup problem and with the necessity of abandoning many water supply wells for the foreseeable future.

The U.S. Environmental Protection Agency (EPA), through its Hazardous Waste Engineering Research Laboratory's Releases Control Branch (HWERL/RCB), has undertaken a research and development effort to address the problem of leaking underground storage tanks (LUST). One potential approach to removing residual contamination in the unsaturated region (vadose zone) is termed vacuum extraction. This is an in-situ technology (i.e., one that does not require the excavation of contaminated material) in which the soil gas within the unsaturated subsurface zone is pumped out of the soil via an applied vacuum at one or more extraction wells. Pressure gradients are created within the unsaturated zone to induce convective air flow through the porous media.(1,2) As the contaminated soil gas flow is extracted from the ground, clean air from the surface is drawn into the contaminanted zone and volatile contaminants are transferred from the liquid or solid matrix into the soil gas stream. Thus, volatile contaminants, including most gasoline constituents that are present in the soil gas, are removed with the extracted air.

Vacuum extraction systems generally consist of the following components:

o Vacuum extraction wells and manifold.

o Piping and connections.

o Gas/liquid separation devices.

o Vacuum pump and discharge pipe.

o Air pollution control equipment.

BACKGROUND

The site is located in the City of Belleview, Marion County, Florida. Contamination of the city's well field with benzene, toluene, ethylbenzene, and xylenes and its subsequent abandonment prompted an investigation by the Florida Department of Environmental Regulation (FDER).(3,4) As a result of the FDER study, a gasoline service station, located on U.S. Highway 441, was determined to be a potential source of contamination.

Land surface elevations in the City of Belleview range from 98 to 102 feet (ft) above mean sea level (msl) near the Union 76 station to 110 to 115 ft msl at the city well field. The geologic units in central southeastern Marion County form three major hydrologic units: the nonartesian shallow aquifer, the clay confining bed, and the artesian Floridan Aquifer.

The surficial geology in the area of the Union 76 gas station consists of medium to fine sand over laying a clayey sand down to about 15 ft below grade. A confining bed of clay is encountered throughout the area, ranging at depths of 3 to 10 meters. The Floridian Aquifer consists of over 600 meters of limestone, which is a highly porous (cavities) and permeable aquifer system.

FDER conducted the vacuum extraction technology (VET) pilot test program. The Terra Vac, Inc. VET system was selected, and the system was operated from January through August 1987. Results of the testing were presented in a Terra Vac Report.(5) **Figure 1** shows the location of the extraction wells in relation to the underground storage tanks and the gasoline supply lines. A subsurface geologic profile of the site is indicated in **Figure 2.** As indicated in the figure, three of the extraction wells' screens are extended to the weathered limestone, and three are screened in the clayey sands.

EVALUATON OF EPA STUDY

From September 26, 1987 through October 23, 1987, EPA conducted field study to evaluate subsurface conditions and the VET efficiency and operating characteristics. The project began towards the tail-end period of the overall VET operation; most of the gasoline contaminants were already removed.

The EPA site assessment involved the measurement of a wide range of parameters to determine the variation in the subsurface zones before and after the re-application of the Terra Vac vacuum extraction system. The experimental methods used to assess the subsurface zones included the analysis of soil gas, soils, and groundwater for the aromatic components and the determination of the total quantity of aromatic components extracted from the subsurface. Approximately 20 soil gas samples, 20 soil samples and 10 groundwater samples were each analyzed during both the initial and final site characterization.

The evaluation of the vacuum extraction system operation required the addition of several monitoring devices in order to measure the of contaminants that were extracted from the subsurface zones. A series of flow measuring devices, pressure sensors, and temperature measuring devices that would accurately and consistently record the operating parameters of the site was installed. As indicated in **Figure 3,** the flow measuring devices consisted of five Annubar^R instruments inserted in various piping networks and two stainless steel venturi meters. The differential pressures generated from the flow measurement devices were measured using diaphragm type pressure gauges rated at 0-10 inches of water. Flow rate calculation from these devices were made based on the operating pressure and temperature of the system.

The pressure measurements were made at the following locations: each extraction well, the operating vacuum pressure at the flow measuring devices, the differential pressures from the flow rate instruments and the absolute barometric pressure of the atmosphere. Temperature measurements were made throughout the piping network of the Terra Vac^R system.

RESULTS OF EPA SITE ASSESSMENT

An initial assessment of the existing degree of contamination in the subsurface zones was performed in September, 1987 prior to the detailed

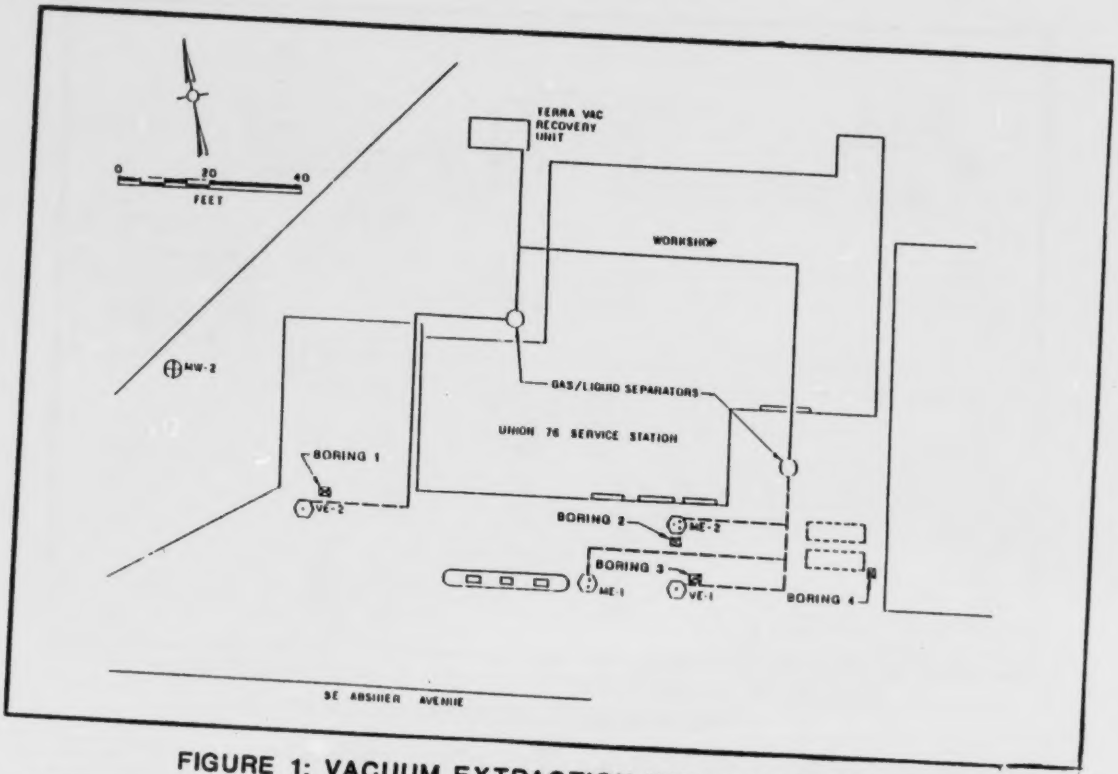

TERRA VAC RECOVERY UNIT
0
20
40
FEET
WORKSHOP
MW-2
GAS/LIQUID SEPARATORS
UNION 76 SERVICE STATION
BORING 1
VE-2
BORING 2
ME-2
BORING 3
ME-1
VE-1
BORING 4
SE ABSHIER AVENUE

FIGURE 1: VACUUM EXTRACTION WELL LOCATION MAP

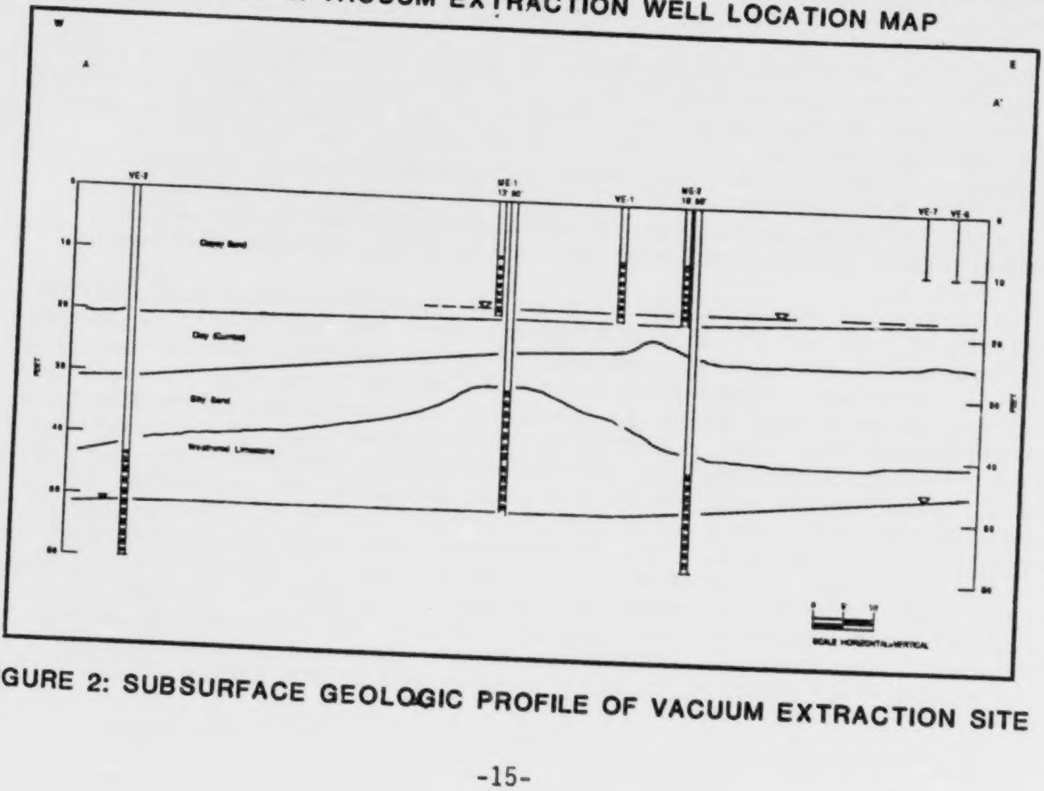

W
A
E
A'
VE-2
ME-1
VE-1
ME-2
VE-7
VE-6
Clayey Sand
Clay (Gumbo)
Silty Sand
Weathered Limestone
FEET
0
10
20
30
40
50
60
SCALE HORIZONTAL=VERTICAL

FIGURE 2: SUBSURFACE GEOLOGIC PROFILE OF VACUUM EXTRACTION SITE

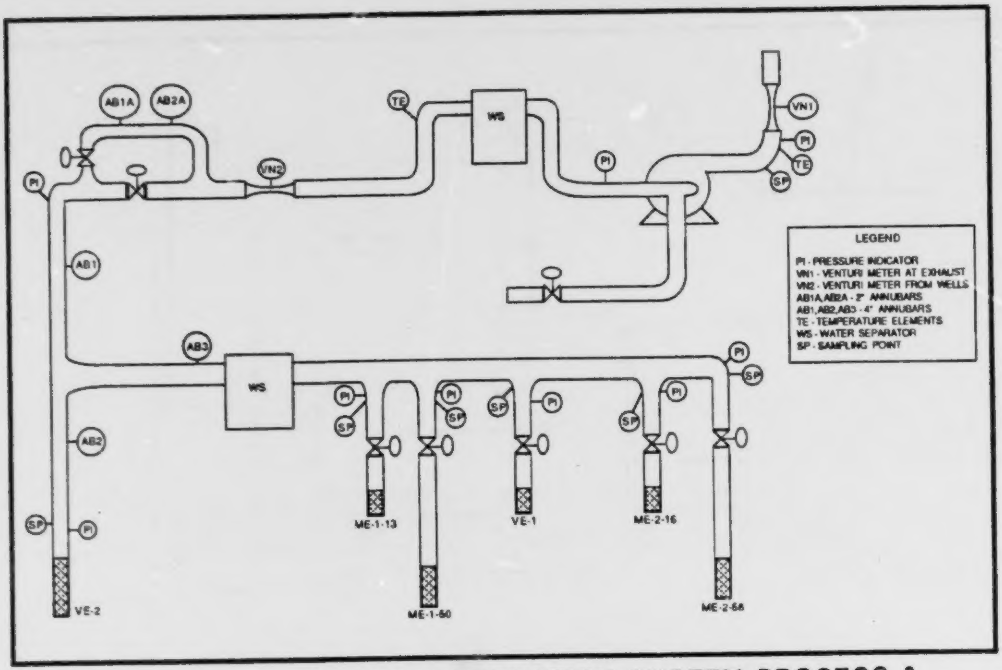

AB1A
AB2A
TE
WS
VN1
PI
TE
SP
VN2
PI
PI
AB1
LEGEND
PI - PRESSURE INDICATOR
VN1 - VENTURI METER AT EXHAUST
VN2 - VENTURI METER FROM WELLS
AB1A,AB2A - 2" ANNUBARS
AB1,AB2,AB3 - 4" ANNUBARS
TE - TEMPERATURE ELEMENTS
WS - WATER SEPARATOR
SP - SAMPLING POINT
AB3
WS
PI
SP
AB2
SP
PI
ME-1-13
VE-1
ME-2-16
VE-2
ME-1-60
ME-2-68

FIGURE 3: VACUUM EXTRACTION SYSTEM PROCESS & INSTRUMENTATION FLOW DIAGRAM

evaluation of the Terra Vac system. This effort consisted of an initial characterization of the site through the data collection activities.

A final site assessment of the existing degree of contamination in the subsurface zones was performed in October, 1987 after 25 days of operation of the vacuum extraction system. Similar to the initial site assessment, this task involved the collection of soil, groundwater, and soil gas samples in order to record the existing characteristics of the site at the end of the detailed evaluation. A comparison of soil data collected by Terra Vac personnel during the installation of the extraction wells (January 1987) and the soil data within this study was also performed.

The experimental methods used to assess the subsurface zones included the analysis of soil gas for aromatic hydrocarbons, the analysis of soils and groundwater for the aromatic components and the determination of the total quantity of aromatic components extracted from the subsurface zones. The soil gas survey consisted of (1) driving a stainless steel probe down to a depth of about four feet, (2) purging up to five volumes of the stainless steel rod with an air sampling pump connected to a gas-tight sampling tap, and (3) sampling the soil gas with a glass gas-tight syringe needle for onsite GC analysis. Soil borings were performed using hollow stem augers and split-spoon samplers. Four samples were taken from each boring down to a depth of 20 feet and shipped offsite for analysis of aromatics using EPA Method 8020. Groundwater sampling consisted of purging up to three well volumes of the groundwater and then hand bailing the well for the sample. The samples were analyzed offsite utilizing a purge and trap extraction (EPA Method 5030) followed by analysis according to EPA Method 8020.

The objectives of the quality assurance efforts for this study were to provide an in-field control program and an evaluation of the measurement data quality. The quality of the measurement data was determined and documented. Precision, accuracy, representativeness, and completeness were evaluated for each sampling media. The soil gas measurements were within the quality assurance guidelines and were determined to be 90% complete. The groundwater data was also determined to be 90% complete. The soil measurements were variable and were determined to be 70% complete.

SOIL GAS SURVEY

Figure 4 depicts a soil gas sampling grid and locations of sampling points. The results of the initial soil gas survey are shown in **Table 1** for benzene (B), toluene(T), ethylbenzene(E), and xylenes(X). Most of the areas surveyed showed no concentration levels above the detection limit of 0.01 ppm for each BTEX component in the surficial soil gas. The areas with elevated concentration levels included the area to the west of the gas station pump island, adjacent to the pump island and to the east of the pump island. The results of the final soil gas survey showed no BTEX concentration levels above the detection level of 0.05 ppm in the surficial soil gas.

GROUND WATER SAMPLING

Figure 5 shows the location of ground water monitoring wells. The results of initial and final sampling are shown in **Table 2**.

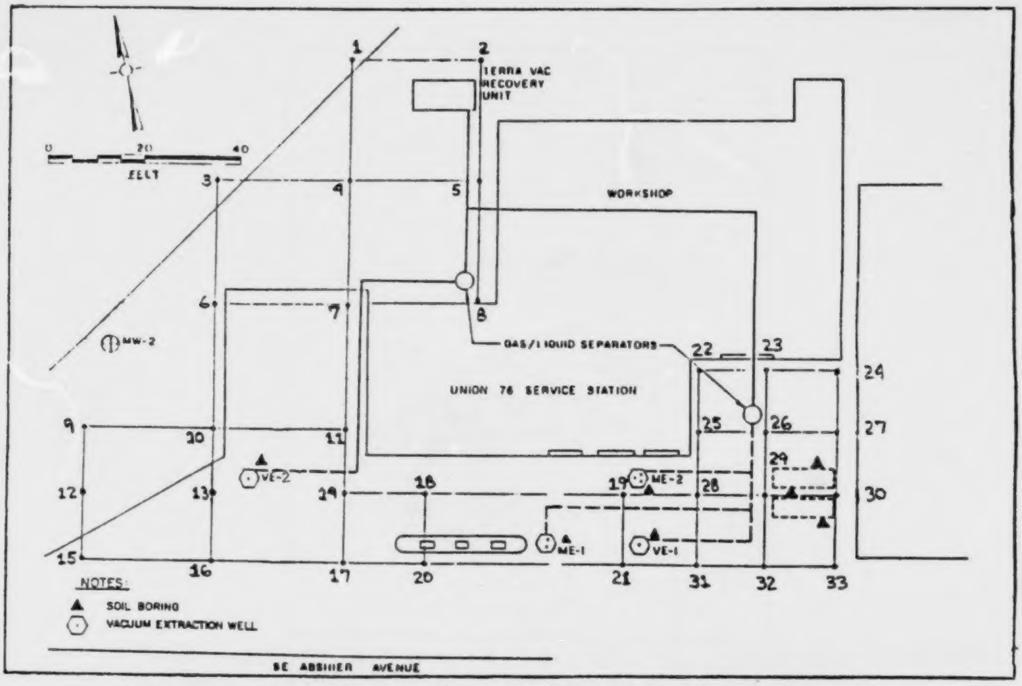

0
20
40
FEET
1
2
TERRA VAC
RECOVERY
UNIT
3
4
5
WORKSHOP
6
7
8
MW-2
GAS/LIQUID SEPARATORS
22
23
24
UNION 76 SERVICE STATION
9
10
11
25
26
27
VE-2
29
ME-2
28
12
13
19
18
19
30
ME-1
VE-1
15
16
17
20
21
31
32
33
NOTES:
SOIL BORING
VACUUM EXTRACTION WELL
SE ABSHIER AVENUE

FIGURE 4: SOIL GAS SAMPLING GRID AND SOIL BORINGS

TABLE 1
SUMMARY OF SOIL GAS SURVEY 9/87

Soil Gas Location	Benzene	Toluene	Ethylbenzene	Xylene
SG3	ND	ND	ND	ND
SG6	ND	ND	ND	ND
SG7	ND	ND	ND	ND
SG9	ND	ND	ND	ND
SG12	ND	ND	ND	ND
SG14	ND	0.06	ND	0.05
SG15	ND	0.03	0.04	0.03
SG16	ND	ND	ND	ND
SG17	ND	ND	0.12	ND
SG18	ND	0.05	ND	ND
SG18	ND	0.45	0.02	0.21
SG19	0.24	0.10	ND	ND
SG20	ND	ND	ND	ND
SG21	0.64	0.30	0.08	ND
SG25	ND	0.02	ND	ND
SG30	ND	0.02	ND	ND
SG31	0.15	0.18	0.02	ND
SG33	ND	0.04	0.12	0.22
SG34	ND	ND	ND	ND
SG35	ND	ND	ND	ND

Notes: All values in ppm (v/v) unless otherwise noted. ND = not detected above 0.01 ppm

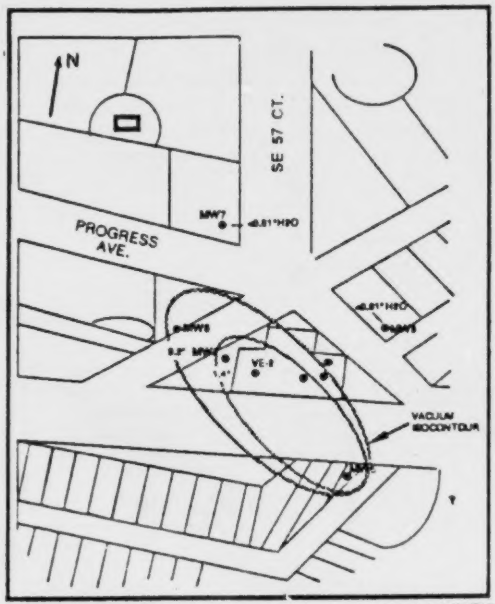

N
SE 57 CT.
PROGRESS AVE.
MW7
<0.01" H2O
<0.01" H2O
MW8
0.2" MW
1.4"
VE-2
VACUUM ISOCONTOUR

FIGURE 5: LOCATION OF GROUNDWATER MONITORING WELLS AND VACUUM TRANSMISSION FROM WELL VE-2

TABLE 2

GROUNDWATER QUALITY DATA

	MW2	MW5	MW6	MW7	MW8
Benzene					
9/25/87	170	BDL	1200	690	BDL
10/25/87	90	BDL	630	500	BDL
Ethyl-benzene					
9/25/87	51	BDL	1200	1200	BDL
10/25/87	0.8	BDL	250	600	BDL
Toluene					
9/25/87	24.0	BDL	830	1.0	BDL
10/25/87	8.0	BDL	580	BDL	BDL
Xylenes					
9/25/87	260	BDL	7200	350	BDL
10/25/87	BDL	BDL	9300	600	BDL

NOTES: All concentrations in micrograms per liter (ug/L). BDL = Below Detection Limit of 1.0 ug/L

The monitoring well MW6 contained about 10,400 ppb of total BTEX in the initial sampling round and about 10,700 ppb (October 1987) of total BTEX in the final sampling round. A comparison between each BTEX component shows a relative decrease for both benzene and ethylbenzene and a relative increase for xylenes, while toluene remained unchanged.

The overall concentrations of BTEX from MW2 and MW6 shows a relative decreased. Benzene, the most volatile component of BTEX, showed the most dramatic decrease. Benzene decreased by about 50% in both wells during the study period.

SOIL SAMPLING

Soil sampling was undertaken to determine the residual of contaminants after eight months operation of the Terra Vac vacuum extraction system. The soil matrix characteristics may vary considerably depending upon the soil type, structure and moisture content. Soil borings were conducted at the Belleview site both before and after the operation of the vacuum extraction system to determine the variation in the soil matrix due to the treatment process. Figure 4 indicates the location of soil borings. Locations of the borings were based upon the existing extraction well locations.

From the initial soil sampling in September, 1987, the highest concentrations for total BETX was found to be about 12 ug/g, near VE-2 at the depth of 4-5 meters. The soil boring near extraction wells ME-2 also showed high concentration levels for total BTEX with about 6.5 ug/g at the 10 foot depth. Additionally, the soil sampling near VE-1 contained the lowest concentration of total BTEX as compared to the other soil borings.

The highest soil concentrations for total BTEX from the final soil sampling program was found to be about 4.5 ug/g near VE-1 at a depth of 8-10 feet. The soil boring near extraction well VE-2 showed concentration levels of about 2.5 ug/g for total BTEX at a depth of 18-20 feet. Additionally the soil sampling near ME-2 showed concentration levels of about 4.0 ug/g for total BTEX at a depth of 13-15 feet. The soil samples taken during the final soil sampling program generally, showed lower contamination as BTEX than the soil samples collected during the initial soil sampling program based on all the soil boring samples, except benzene which showed an increase in concentration. The soil concentrations from the initial soil borings had mean concentration levels of 0.22 ug/g for benzene, 0.26 ug/g for toluene, 0.47 ug/g for ethylbenzene and 1.34 ug/ug for xylenes. The soil concentrations from the final soil borings had mean concentration levels of 0.52 ug/g for benzene, 0.17 ug/g for toluene, 0.28 ug/g for ethylbenzene, and 1.13 ug/g for xylenes.

RESULTS OF EPA FIELD EVALUATION OF VET SYSTEM

The operational conditions of the Terra Vac system were evaluated through the measurement of pressure, temperature, gas flow rates, and soil gas concentrations in the piping network. The results of the onsite flow measurements and contaminant analyses, during the 23 days of the vacuum extraction operation, are presented in the following sections.

Contaminant concentrations in gas stream in each of the extraction wells were measured at least once each working day for the four week period from September 27, to October 23, 1987. Each sample was analyzed for benzene(B), toluene(T), ethylbenzene(E), xylenes(X), and total hydrocarbons(THC) as previously described. The total hydrocarbon and BTEX concentration trends for all extraction wells appeared to decrease over time. **Figures 6 and 7** illustrate these trends for wells VE-1 and ME-1-50, respectively and they are representative of the extraction gas profiles from the other extraction wells.

A statistical analysis of the concentration data over time, using the Mann-Kendall test for trend, confirmed the trend for wells VE-1 and ME-1-50. The test indicated a downward trend for the operated extraction wells within a 90% confidence level. The Mann-Kendall test is a nonparametric test for zero slope of a linear regression of time-ordered data versus time(6). The relative degree of a trend is presented by the value of test result in either the negative or positive direction. **Tables 3 and 4** present the results of the Mann-Kendall test.

The gas extraction flow rates for individual wells were estimated as a function of the measured vacuum at each well due to the underground construction of the piping. Individual well flow rates could not be measured simultaneously during the study. A linear correlation between each well and the section Venturi meter was developed from the total system flow measurements. The flow rate measurements from the system were measured by sequentially shutting off one well at a time and remeasuring the total flow until all but one well was on.

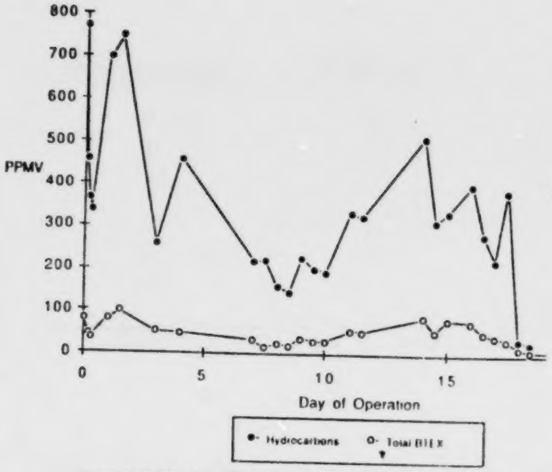


FIGURE 6: EXTRACTION GAS CONCENTRATION FROM WELL VE-1

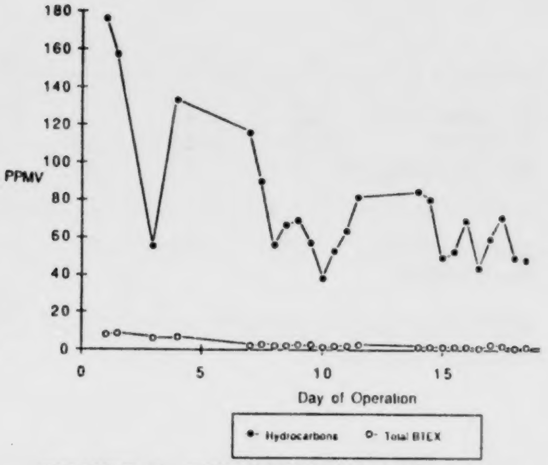


FIGURE 7: EXTRACTION GAS CONCENTRATION FROM WELL ME-1-50

TABLE 3
EXTRACTION GAS CONCENTRATIONS FROM WELL VE-1

Concentrations in PPMV

	B	T	E	X	Total BTEX	Hydrocarbons
Minimum*	0.13	1.67	0.13	1.25	3.63	28.40
Maximum	30.80	39.21	3.52	63.20	99.64	771.60
No. of Samples	28	28	28	28	28	26
Mann-Kendall Trend Test	-202	-182	-67	14	-100	-121

*All Statistics calculated for days of constant flow conditions (9/28 through 10/20)

The deep extraction wells produced higher gas flows at a given vacuum than did the shallow wells due to the difference in soil types. Although all of the wells were operated under approximately 150 centimeters of water vacuum, the flows varied from 283 to 6,500 slpm[+] between the shallow (ME-1-13) and deep extraction (ME-1-50) wells.

The rate at which contaminant mass was extracted from each well was calculated as a product of the gas flow rate and the contaminant concentration for each sampling event for each well. Since the flows were

---

[+] standard liters per minute

TABLE 4
EXTRACTION GAS CONCENTRATIONS FROM WELL ME-1-50

Concentrations in PPMV

	B	T	E	X	Total BETX	Hydrocarbons
Minimum*	0.21	0.43	0.05	0.56	1.34	38.6
Maximum	0.88	2.84	0.18	5.00	8.77	176.0
No. of Samples	27	27	27	27	27	24
Mann-Kendall Trend Test	-152	-182	-54	-194	-173	-88

*All Statistics calculated for days of constant flow conditions (9/28 through 10/20)

controlled by the vacuum pump at a relative constant rate, extraction rates generally fluctuated in a similar manner as the concentrations. Even though VE-1 had higher soil gas concentrations than ME-1-50, the low air flow rate produced a smaller contaminant extraction rate.

VACUUM TRANSMISSION

As part of the EPA field VET study, an evaluation of the vacuum transmission throughout the vertical and horizontal extent of the site was conducted by measuring the induced vacuum at monitoring wells and soil-gas locations. All monitoring well screens were extended both in and above the water table which enabled the measurement of vacuums in the unsaturated zone just above the water table. Monitoring wells MW2, MW5, MW6, MW7 and MW8 were sealed to the atmosphere and pressure measuring devices were connected to the casing to measure the vacuum.

The horizontal extent of the transmitted vacuum is shown in Figure 5 when only extraction well VE-2 is open (all other wells closed) and operating at a vacuum of 30 centimeters of water. The transmitted vacuum profile from both illustrations shows an elliptical shape around the extraction wells with the major extent of the isocontour directed toward the southeast near monitoring well MW5. The vacuum observed from MW2, which was 12 meters from extraction well VE-2, were almost identical to those observed from monitoring well MW5, even though MW5 is about 55 meters away from the extraction well. The transmitted vacuum in MW2 and MW5 were about 10% of the applied well head vacuum. These observations indicate that more air flow is entering VE-2 from the southeast direction from MW5 than the air flow entering from the northeast direction from MW2. In other words, a larger fraction of the air flow extracted from VE-2 is pumped from the southeast direction. The vacuum profile shows a different flow pattern of the contaminants as compared with the groundwater plume which showed a flow pattern from the source in a northwest direction.

CONCLUSIONS

During the EPA field VET study at the Belleview site, the vacuum extraction system was modified with specific instrumentation to measure air flow rates, vacuum pressures and air stream temperatures. The instrumentation provided data on the daily system operating conditions, which were used to calculate flow rate measurements and contaminant mass extraction rates.

Benzene, toluene, ethylbenzene and xylenes were removed in significant quantities from the application of the vacuum extraction system to the subsurface zones. In this system, although the EPA field study began at the tail-end of the FDER's pilot cleanup operation, a total of 10 kg of BTEX was removed during the 25-day test period of this study.

In addition to the BTEX removed, other major volatile gasoline components were removed. The total hydrocarbons, as BTEX equivalent, removed were approximately 90 kg in the same period.

The quantity of contaminants extracted from each extraction well varied greatly over the spatial distribution of the site. In general, the shallow extraction wells located in the clayey sands exhibited significantly higher extracted soil gas concentrations than observed from the deep extraction wells located in the weathered limestone formation. However, the deep extraction wells exhibited significantly greater air flow rates than the shallow extraction wells when the same vacuum was applied at the well head. The net result of this combination of soil gas concentration and the air flow rate, the BTEX extraction rate, demonstrated that the deep extraction wells extracted more mass of contaminants (approximately 70% of the total mass extracted) than the shallow extraction wells did, even though the relative contamination was greater in the clayey sands.

ACKNOWLEDGEMENTS

The VET facilities and equipment operation were supported by the Florida Department of Environmental Regulation (FDER) and Terra Vac, Inc. and their cooperation was greatly appreciated. This VET assessment was funded by the EPA Hazardous Waste Engineering Research Laboratory (HWERL). The authors extend their sincere thanks to the members of the FDER Bureau of Waste Cleanup and the colleagues in the HWERL Releases Control Branch and at CDM for their advice and assistance.

REFERENCES

1. Carlson, J. Recovery of Landfill Gas at Mountainview: Engineering Site Study, U.S. EPA EPA-530/SW-587d, Washington, DC, 1977.

2. R.F. Weston, Inc., Task 11. In Situ Air Stripping of Soils Pilot Study, U.S. Army Toxic & Hazardous Material Agency, AMXTH-TE-TR-85026, Aberdeen, MD, 1985.

3. E.S.E. Inc., Belleview Contamination Assessment Draft Report, Florida Department of Environmental Regulations, ESE No. 84-521-0200-2140, Tallahassee, Florida, December 1984.

4. E.S.E. Inc., Additional Contamination Assessment Belleview/Union 76 Site Belleview Florida, Florida Department of Environmental Regulations, ESE No. 87-207-0100-2150, Tallahassee, Florida, July 1987.

5. Terra Vac Corp., Union 76 Gas Station Clean-up, Belleview, Florida, Florida Department of Environmental Regulation, Bureau of Operations, Tallahassee, Florida, August 1987.

6. Gilbert, Richard O., Statistical Methods for Environmental Monitoring, Van Nostrand Reinhold Co., New York, 1987

Disclaimer: Mention of trade names or commercial products does not constitute recommendation for use, and no EPA official endorsement should be inferred.

DISCOVERY OF A NEW SOURCE OF ERROR IN TIGHTNESS TESTS ON OVERFILLED TANKS

Robert D. Roach, James W. Starr, Christopher P. Wilson, Daniel Naar,
Scott Reed, Joseph W. Maresca, Jr.
Vista Research, Inc.
Mountain View, California 94042
John S. Farlow
U. S. Environmental Protection Agency
Edison, New Jersey 08837

ABSTRACT

Experiments conducted at EPA's HWERL Underground Storage Tank (UST) Test Apparatus in Edison, New Jersey, have uncovered a major flaw in the protocol of most overfilled-tank test methods. Most of these methods attempt to interpret product-level changes in the fill tube (or standpipe) as product volume changes. This interpretation can be seriously in error because any volume change induces a product-level (or head) change, which in turn induces a tank deformation (or tank capacity) change having the opposite sense of the original volume change. As a consequence, the measured volume changes are always smaller than the true volume changes. Large errors may result because of these fill-tube dynamics. The fundamental algorithm used to estimate the temperature-compensated volume rate and the current practice of waiting for the structural deformation effects to become small enough to be negligible are not valid, and will not work unless the tank is absolutely rigid and does not deform.

A mathematical model has been developed and validated to quantify this complex interaction and to develop a means for solving the problem. The model and experimental data show that the magnitude of the error is a function of the fill tube's cross-sectional area, the tank's elasticity constant, the tank's deformation time constant, the volume of trapped vapor, and the height-to-volume constant. Furthermore, a correct interpretation of the volume changes during a measurement requires that the temporal history of the product level be known *a priori*, since the magnitude of future volume change depends on the magnitude of past product-level changes.

The error can be minimized if product volume measurements are made at a constant pressure head. This could be accomplished in an overfilled-tank tightness test by periodically releveling the product in the fill tube and measuring volume directly. If properly done, the volume change induced by temperature changes can be determined and can be subtracted directly from the measured volume changes, after waiting for the initial volume changes due to deformation to become small. The waiting time must be increased if the releveling is not done continuously during a test. For example, model calculations indicate that the waiting period will increase by approximately 14% if the product is releveled at 15-min intervals.

Tightness tests in partially filled tanks are not affected by this error, since the mean changes in product head measured during a test are usually very small.

INTRODUCTION

The U. S. Environmental Protection Agency (EPA) has evaluated the performance of 25 volumetric methods for detecting leaks in underground storage tanks (UST) containing unleaded gasoline. The evaluations were performed by the Hazardous Waste Engineering Research Laboratory (HWERL) at EPA's Underground Storage Tank (UST) Test Apparatus located in Edison, New Jersey. The results of the program are described in (1).

OVERVIEW OF A VOLUMETRIC TEST

A volumetric leak detection method (also known as a precision test or a tank tightness test) attempts to measure the change in product level (and to interpret it as product volume change) that results from a leak in the tank. Most methods measure both product level and product temperature. The product-level changes are converted to volume using a height-to-volume calibration factor (A_{eff}), and the temperature changes are converted to volume using estimates of the coefficient of thermal expansion and of the volume of the product in the tank. A temperature-compensated flow rate is estimated by subtracting the temperature-induced volume changes from the measured volume changes. The temperature-compensated volume rate is then compared to a threshold leak rate to determine whether the tank should be declared leaking or not. If the measured volume rate exceeds the threshold, the tank is declared leaking.

MISINTERPRETATION OF PRODUCT-LEVEL MEASUREMENTS IN OVERFILLED TANKS

The underlying assumption of a volumetric test is that product-level changes in a tank produced by a leak, as well as any other volume changes, such as thermal expansion or contraction of the product, can be related to product-volume changes using A_{eff}. Analysis of data collected on product level and product temperature in the fill tube of an overfilled tank (Figure 1) at the UST Test Apparatus indicated that product-volume changes could not be estimated from the product-level changes using A_{eff}. This calibration problem was not observed during the experiments conducted in partially filled tanks, or those in overfilled tanks in which the volume of product required to maintain a constant level in the fill tube was measured directly.

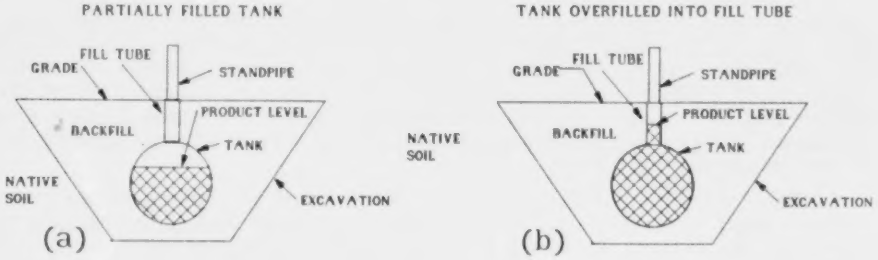


Figure 1. Cross-sectional view of an underground storage tank that is (a) partially filled and (b) overfilled into the fill tube.

It was hypothesized that the structural deformation of the tank produced by the product-level changes in the fill tube during the tests was responsible for the error. Because of the small cross-sectional area of the fill tube, even small volume changes will produce product-level changes (and, therefore, pressure changes) large enough to deform the tank.

STRUCTURAL DEFORMATION OF AN UNDERGROUND STORAGE TANK

If the tank-backfill-soil system is elastic, the tank will deform in response to any product-level change. The structural deformation that occurs when the product level is changed in the fill tube of an overfilled tank consists of two effects: an instantaneous deformation and a time-dependent, exponential relaxation. Measurements at the UST Test Apparatus have suggested that the tank will deform instantaneously in response to any product-level change. The instantaneous deformation of the tank appears to be an elastic effect, because the volume change produced by a rise in the product level is identical to that produced by a drop of the same magnitude. This volume change is observed in both steel and fiberglass tanks, and is thought to be primarily caused by the elastic properties of the gravel backfill around the tanks. Because of the instantaneous deformation, the product-level change expected (based on a known volume change) will be less than what would be expected based on geometrical considerations, and is included in the measurement of A_{eff}. The height-to-volume calibration factor (volume change per unit of height change), A_{eff}, is defined by

$$A_{eff} = A + A_{isd} + A_{vp} \tag{1}$$

where A is the free surface area of the product, A_{isd} and A_{vp} are the volume change per unit of product-level change produced by the instantaneous structural deformation of the tank and the compressibility of trapped vapor, respectively. An estimate of A_{eff} is made by measuring the product-level changes produced by inserting and removing a bar of known volume. A_{isd} and A_{vp} cannot be measured separately unless the volume of the trapped vapor is known.

For a partially-filled-tank test, A_{eff} (i.e., $A_{vp} = A_{isd} = 0$) is primarily a function of the tank geometry, which can be estimated from the cross-sectional surface area of the product surface (A) in the tank during a test. This is usually done using an accurate tank chart and a measurement of the product depth. For a tank overfilled into the fill tube or standpipe, however, A may not be accurately known, because the number, size, and location of the underground tubes and piping are often unknown. Even if the A were known, this estimate of A_{eff} would not be accurate in an overfilled-tank test, because the magnitude of A_{eff} is affected by A_{isd} and A_{vp}. In overfilled-tank tests, consequently, the value of A_{eff} must be measured. It is also advisable to measure A in a partially-filled-tank test in case the tank chart is in error.

After the instantaneous deformation, an exponential, time-dependent relaxation of the tank occurs. This exponential relaxation is produced by the consolidation of the native soil and of the backfill in the excavation. In a test with constant hydrostatic pressure, the volume changes associated with the exponential relaxation will eventually become small, and accurate estimates of the volume changes produced by a leak or by other effects can be made. If the hydrostatic pressure is not kept constant during the test, the tank will deform in response to every successive change in the hydrostatic pressure. The deformation of the tank will result in a volume change of the product in the tank, but in an opposite sense to the original volume change. The product-level changes in the fill tube that are produced by a leak, as well as by expansion or contraction of the product and trapped vapor, interact in a complex feedback loop in such a way as to the deform the tank. This dynamic interaction results in volume changes which are always less than would be expected from the true product volume changes alone.

A mathematical model was developed and validated to quantify the fill-tube dynamics. The model and the experimental data collected at the UST Test Apparatus show that the product-level changes as a function of time are a function of the fill tube's cross-sectional area (A), the tank's elasticity constant (K), the tank's time constant (T), the volume of trapped vapor (V_{vapor}), and the height-to-volume constant (A_{eff}). The values of K, T, V_{vapor}, and A_{eff} must be known (i.e., measured) for the tank being tested if product-level changes are being measured. Furthermore, a correct interpretation of the volume changes during a measurement requires that the temporal history of the product-level changes be known a priori, since the magnitude of future volume changes depends on the magnitude of past product-level changes.

OBJECTIVE

The objective of this paper is to develop and validate a model that quantitatively describes the dynamics of the product-level interactions in the fill tube of an overfilled tank. The model is used to investigate three common product-level scenarios: (1) the product-level changes that occur as a result of topping the tank, (2) the product-level changes that occur in the fill tube in response to a leak or any other volume change, and (3) the product-level changes that occur when the product in the fill tube is periodically releveled to maintain a constant hydrostatic pressure during a test. The model suggests three possible ways of minimizing the potential error.

FILL-TUBE DYNAMICS MODEL

When product is brought into the fill tube (or an above-grade standpipe) of an underground storage tank, the resultant increase in the hydrostatic pressure causes the tank to expand. The increase in tank volume produced by the tank expansion lowers the product level in the fill tube. The tank will now relax towards an equilibrium level that is changing. Similarly, when product is removed from the fill tube, the decrease in the hydrostatic pressure will cause the tank to contract and the product level in the fill tube will rise. This expansion and contraction of the tank volume is strongly dependent on the compressibility of the backfill in the excavation and the native soil surrounding the excavation.

PRODUCT-LEVEL MEASUREMENTS IN OVERFILLED TANKS

An exponential relaxation model is hypothesized to describe the volume and product-level changes produced by tank deformation in an overfilled tank. The model is mathematically derived first for the specific case of instantaneously adding a known amount of product, ΔV_p, to a tank initially overfilled into the fill tube, where the volume of the product in the tank, fill tube and standpipe, $V_p(t)$, as a function of time, t, is assumed to be greater than the volume of the tank, V(t). This model describes the product-level changes produced by topping the tank, a procedure used by most methods in order to reach the product level required to start a tank test. The model formulation does not include an estimate of the change in the flow rate of a leak produced by a change in the hydrostatic head. This addition of product results in an instantaneous rise, Δh, in the product level in the fill tube. The model assumes an exponential increase in the volume of the tank itself. This is described by

$$V(t) = V_o + K\,\Delta h\left(1 - e^{-(t-t_o)/T}\right) \qquad (2)$$

for $t \geq t_o$ where V_o is the volume of the tank at t_o, t_o is the time that the product level is instantaneously changed by Δh; K is the equilibrium elasticity of the tank-backfill-soil system; and T is the constant hydrostatic pressure relaxation time constant of the tank-backfill-soil system.

The rate of change of the volume of the tank with respect to time for $t \geq t_o$ is given by

$$\frac{dV(t)}{dt} = \frac{K\,\Delta h}{T}\,e^{-(t-t_o)/T} \quad , \qquad (3)$$

where $dh/dt = \Delta h\,\delta(t-t_o)$, and $dV(t)/dt = 0$ for $t < t_o$, and where $\delta(t-t_o)$ is the Dirac delta function.

The product-level changes in the fill tube are estimated by

$$h(t) = \frac{(V_p(t) - V(t))}{A_{eff}} \qquad (4)$$

where $V_p(t) > V(t)$.

It is assumed that the volume changes produced by all product-level changes will add by linear superposition. This means that the total volume change can be computed by adding all of the individual volume changes produced by each instantaneous product-level change. This is given mathematically by the convolution integral

$$\frac{dV(t)}{dt} = \frac{K}{T}\int_{-\infty}^{t} \frac{dh(\tau)}{dt} e^{-(t-\tau)/T} d\tau \tag{5}$$

where τ is the time variable of integration. Eq. (5) can be expressed as

$$\frac{dV(t)}{dt} = \frac{K}{T}\left(\frac{dh(t)}{dt} * \omega\right) \tag{6}$$

where * indicates the convolution between dh(t)/dt and ω, with $\omega = 0$ for $t < 0$ and $\omega = \exp(-t/T)$ for $t \geq 0$. The rate of change of the product level that results after differentiating Eq. (4) with respect to time and substituting Eq. (6) is

$$\frac{dh(t)}{dt} = \frac{1}{A_{eff}}\left(\frac{dV_p(t)}{dt}\right) - \frac{K}{A_{eff}T}\left(\frac{dh(t)}{dt} * \omega\right) \tag{7}$$

where

$$\frac{dV_p(t)}{dt} = \Delta V_p \delta(t-t_o) \tag{8}$$

and $\delta(t-t_o)$ is the Dirac delta function. Eq. (7) can be solved via Fourier Transform methods and integrated from $-\infty$ to time t to give the product-level time series for $t \geq t_o$

$$h(t) = \frac{\Delta V_p}{A_{eff}} + \frac{\Delta V_p}{A_{eff}}\left(\frac{K}{A_{eff}+K}\right)\left(e^{-(t-t_o)/T_{eff}} - 1\right) \tag{9}$$

where the effective time constant of the tank is defined by

$$T_{eff} = T\frac{A_{eff}}{(A_{eff}+K)} \tag{10}$$

The product-level changes can be converted to product-volume changes by multiplying by the effective cross-sectional area, A_{eff}. The first term in Eq. (9) is the product-level change caused by the sum of the effects of the instantaneous deformation of the tank and of any trapped vapor. The magnitude of the instantaneous deformation is determined by the magnitude of the effective cross-sectional area of the fill tube. The second term is the relaxation due to tank deformation. The time it takes for the tank to deform is determined by T_{eff}, the effective time constant of the tank. Eq. (10) suggests that the effective time constant is always shorter than the time constant in a constant-head test (i.e., time constant of the tank itself), and is a function of A_{eff} and the unknown elasticity constant, K, of the tank-backfill-soil system.

Table 1 presents the values of the effective time constant, T_{eff}, for different values of A_{eff} and K, where it can be assumed that A_{eff} is mainly a function of the fill tube cross-sectional area, A. The values of T and K are within the range of values estimated experimentally for the steel and fiberglass tanks at the UST Test Apparatus. For fill tubes of small diameter, the deformation occurs very quickly in comparison to those with large diameters. The calculation suggests that a fill tube with a diameter of 81 cm (32 in.) has a time constant approximately equal to that of the tank.

The product level at infinity (i.e., many hours after the initial deformation) is given by

$$h(\infty) = \frac{\Delta V_p}{A_{eff}+K} \tag{11}$$

The total height change in the fill tube is interpreted in terms of the long-term height-to-volume calibration constant, $(A_{eff} + K)$, rather than the short-term calibration constant, A_{eff}. An estimate of $h(\infty)$ cannot be made unless the elasticity constant of the tank is known. The total drop in product in the fill tube is

$$h(t_o) - h(\infty) = \frac{\Delta V_p}{A_{eff}} - \frac{\Delta V_p}{A_{eff} + K} \qquad (12)$$

For small K, $[h(t_o) - h(\infty)]$ is approximately zero.

TABLE 1. ESTIMATE OF HOW T_{eff} CHANGES WITH A_{eff} and K*

Effective Fill Tube Diamater (cm)	A_{eff} (cm^2)	K (cm^2)	T_{eff} (h)
10.2	81.1	120	0.40
10.2	81.1	60	0.57
10.2	81.1	30	0.73
10.2	81.1	15	0.84
5.1	20.3	120	0.14
20.3	324.3	120	0.73
40.6	1297.2	120	0.92
81.2	5188.7	120	0.98

* Eq. (10) is used to make the predictions using T = 1 h for a 1-m rise in product level prior to starting a tank test.

Eq. (7) can be generalized to predict the product-level changes produced by any type of product-volume change as opposed to just the instantaneous volume change used to derive Eq. (9). The product-level changes that result are given by

$$h(t) = \frac{V_p(t)}{A_{eff}} - \frac{K}{A_{eff}^2 T} \int_{-\infty}^{t} V_p(\tau) e^{-(t-\tau)/T_{eff}} d\tau \qquad (13)$$

The product-volume changes in the fill tube can be estimated by multiplying Eq. (13) by A_{eff}.

Eq. (13) indicates that the product-level changes in the tank at any point in time are affected by the product-level changes that occurred in the past. Thus, in order to interpret the current product-level changes in terms of volume, the past product-level changes must be known and included. It is also clear from Eq. (13) that the procedure for topping the tank will affect the product-level changes. The deformation of the tank and the resulting product-level changes will be different if the same volume of product is added to the tank but at a different rate or in different amounts. While in this case the product-level and product-volume changes were defined as zero for the period before the product was added, this is not necessarily true in other situations. It is important to follow the same topping procedure to maintain a predictable performance.

If the rate of change of volume of the product in the tank is a constant, C, then it can be shown that the rate of change of the product level in the tank is given by

$$\frac{dh(t)}{dt} = \frac{C}{A_{eff} + K} \qquad (14)$$

where C is the flow rate produced by a leak, or any other product volume change. C is equal to the leak rate, L, if all other volume changes are equal to zero. A negative leak rate or volume rate is defined as flow out of or a decrease in the volume of the product in the tank. In the fill tube, a leak which produces a constant rate of change of product volume produces a product-level change which can not be estimated from A_{eff} unless K is zero. To estimate C using Eq. (14), an estimate of the long-term height-to-volume calibration factor, $A_{eff} + K$, is required. Since K is generally unknown during an actual test, C can not be accurately estimated. If K is equal in magnitude to A_{eff}, then the measured product-level change and, therefore, the product-volume change obtained by multiplying the product-level changes by the measured height-to-volume conversion factor may be too small by a factor of 2 or more. In a partially filled tank, the product-level changes can be directly related to volume by the height-to-volume estimated from a tank chart because ($A_{eff} = A$) >> K. For a partially filled tank Eq. (14) reduces to

$$\frac{dh(t)}{dt} = \frac{C}{A} \qquad (15)$$

Eq. (14) also demonstrates that the effects of deformation are important and will occur even if there are no deliberate, operator-initiated product-level changes as assumed in the derivation of Eq. (9). Any change of volume, whether it be a leak or thermally induced expansion or contraction of the product, will affect the measured product-level changes similarly.

Finally, consider the case in which the product level is instantaneously raised in the fill tube when the rate of change of volume in the tank is a constant. This is described mathematically by

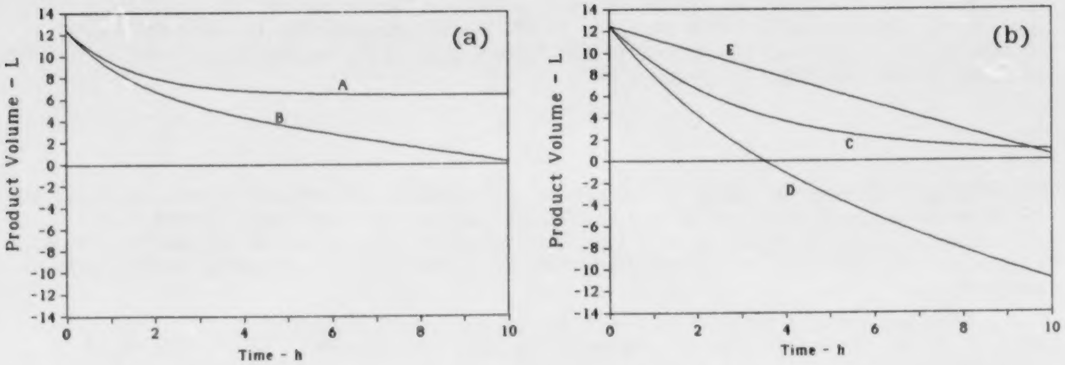
$$h(t) = \frac{\Delta V_p}{A_{eff}} + \frac{\Delta V_p}{A_{eff}}\left(\frac{K}{A_{eff} + K}\right)\left(e^{-(t-t_o)/T_{eff}} - 1\right) + \left(\frac{C(t - t_o)}{A_{eff} + K}\right) \qquad (16)$$

Eq. (16) predicts the product-level changes that would occur in a leaking tank, or a tank in which the product volume is changing, when a volumetric test is initiated by topping the tank. The product-level change consists of a large exponential change in the product level, followed by a linear rate of change. The linear rate of change predicted by Eq. (16) after several time constants, T_{eff}, have elapsed is identical to Eq. (14).

Eq. (16) predicts the product-volume changes in a 10-cm (4-in.) diameter fill tube predicted by Eq. (16) that are produced by a 1-m product-level rise resulting from topping the tank immediately before the start of a test, and by a -1.2 L/h rate of change of volume during the test. The product-volume changes are shown in Figure 2a. The product-level changes are converted to volume changes using A_{eff}. The volume change is assumed to be produced by a leak, thermal contraction of the product, or a combination of these. No other volume changes are considered. Values of $K = 120$ cm², $T = 3$ h, $T_{eff} = 1.5$ h, and $A_{eff} = 125$ cm², typical of the steel tank at the UST Test Apparatus, were used in the calculations. The predicted product-volume change, after several time constants, T_{eff}, have elapsed, is -0.61 L/h, only 51% of the actual -1.2 L/h volume rate. For comparison, the product level changes that are the result of deformation only are also shown in this prediction; the rate of change of volume is zero. This could represent an error of 51% in either the leak rate, the temperature-induced volume changes, or a linear combination of both. If the tank is not leaking, and the volume changes are produced only by temperature changes, the temperature-compensated volume rate obtained by subtracting the measured volume rate of -0.61 L/h from the actual volume rate of -1.2 L/h would be +0.59 L/h instead of zero.

Eq. (16) is also solved for the cases when no deformation occurs (i.e., $K = 0$ cm²), when A_{eff} >> K (i.e., partially-filled tank), and when the volume changes in the tank are zero (i.e., Eq. (9)). All three accurately estimate the actual volume rate. For comparison, these results are plotted on Figure 2b.

The two effects which occur after the tank is topped are significant. First, if a test is conducted too soon after a product-level change, the measurement is typically dominated by the exponential volume change of the tank. Many methods attempt, before starting a test, to wait until the large exponential decay has occurred. Second, it is mistakenly assumed that once the large decrease in product level becomes constant, an accurate test of the tank can be conducted. This is not true if K is approximately equal in magnitude to A_{eff}, because the linear product-level changes that occur after the exponential changes have occurred are only a fraction of the actual product-level changes that would occur if the tank were rigid and did not deform. The effect is particularly severe when the diameter of the fill tube is small, because even large leak rates would produce only small product-level changes.



A: A_{eff} = 125 cm², K = 120 cm², T = 3 h, $C_{predicted} = C_{actual}$ = 0.0 L/h.
B: A_{eff} = 125 cm², K = 120 cm², T = 3 h, $C_{predicted}$ = -0.61 L/h, C_{actual} = -1.2 L/h.
C: A_{eff} = 4560 cm², K = 120 cm², T = 3 h, $C_{predicted} = C_{actual}$ = 0.0 L/h.
D: A_{eff} = 4560 cm², K = 120 cm², T = 3 h, $C_{predicted} = C_{actual}$ = -1.2 L/h.
E: A_{eff} = 4560 cm², K = 0 cm², T = 3 h, $C_{predicted} = C_{actual}$ = -1.2 L/h.

Figure 2. Comparison of the Fill-Tube Dynamics Model predictions using Eq. (16) for different combinations of A_{eff}, K, and C. In a small-diameter fill tube, only a fraction of the actual leak rate is predicted. $C_{predicted}$ is estimated 3 or more time constants after the start of the test.

OVERFILLED-TANK TEST WITH RELEVELING

Some methods measure volume changes directly by periodically adding or removing a measured amount of product to maintain a constant product level in the fill tube. Because product level is kept approximately constant, no significant additional deformation of the tank occurs during the test. The measured volume changes (obtained by using A_{eff} to convert to product-level changes) represent the actual volume changes occurring in the tank.

The model was extended to include the effects of periodically releveling the product in the fill tube every λ min in the presence of a constant volume change, C, where C is the sum of a constant leak rate, L, or any other constant product-volume change not related to a leak. The model includes the topping effect whereby a known amount of product is instantaneously added to the fill tube to attain a specified level for the test. The volume at $t = n\lambda$ required to bring the product level to zero is given by

$$V_n = -C\lambda + \left[\frac{KC}{A_{eff}+K}\left(\lambda - T_{eff} + T_{eff}e^{-\lambda/T_{eff}}\right) - \left(\frac{A_{eff}}{A_{eff}+K}\right)V_p(o)\left(1-e^{-\lambda/T_{eff}}\right)\right] \cdot \left(K + A_{eff}\frac{e^{-\lambda/T_{eff}}}{A_{eff}+K}\right)^{n-1}, n \ge 1 \qquad (17)$$

The derivation of Eq. (17) is mathematically complex and only the result is given here. The analytical solution was compared to the numerical solution generated using Eq. (13) for verification. The total amount of product added to maintain a constant level in the fill tube is obtained by summing the V_n calculated using Eq. (17) for all n. This is equal to the product-volume drop in a fill tube of very large diameter; the drop would be estimated for the same parameters using Eq. (16). If the releveling period is very much smaller than the effective time constant, Eq. (17) is approximated by

$$V_n \cong -C\lambda - V_p(o)\frac{\lambda}{T}e^{-(n-1)\lambda/T} \qquad (18)$$

In practice, $V_p(0)$ is unknown because the time history of past volume changes is unknown. It is assumed that the product level is constant (i.e., no volume changes), $-h_o$, for all time $t < 0$, and is then raised a constant amount, h_o, at $t = 0$. It can then be shown that

$$V_p(o) = -Kh_o \tag{19}$$

Thus, the volume change of the product at $t = 0$ is dependent on the value of K, which is not known under most testing conditions.

If the product in the fill tube is releveled continuously, then the volume changes will be equal to the leak rate after the deformation produced by an initial addition of product to the tank has ceased. The constant hydrostatic pressure time constant governs the deformation. The volume changes predicted by Eq. (17) are approximately equal to those shown in Figure 2b when Eq. (16) for the calculation made with $A_{eff} = 4560\ cm^2 >> K = 120\ cm^2$, providing that the product is releveled almost continuously. If the tank is releveled every 15 min, the time constant of the volume changes is approximately 1.14 T. This was obtained by solving Eq. (17) and computing the time constant directly. Thus, the penalty for not releveling continuously is a small increase in the time required to test a tank.

SUMMARY

Any product-level change will deform the tank. Tests which allow the product level in the fill tube or in a standpipe to change freely may be subject to serious errors, because product-volume changes are not accurately estimated from the product-level changes in the fill tube using A_{eff} when $K >> 0\ cm^2$ or when $K >> A_{eff}$. While T is also unknown, its exponential behavior is known, and an algorithm can be developed to minimize this effect by waiting for the volume changes to become negligible. The actual or true volume changes can be obtained by multiplying by the long-term volume-to-height conversion factor (i.e., $A_{eff} + K$) once the exponential changes induced by product-level adjustments necessary to start a test have become small. The magnitude of the error will depend on the elasticity of the tank. Since K is unknown, accurate estimates of the actual volume rate are difficult to make. If A_{eff} is not measured, then the error is larger yet. If K happens to be small compared to A_{eff}, the error is also small, but the tester has no way to know this.

EXPERIMENTS AT THE UST TEST APPARATUS

Experiments were conducted at EPA's HWERL UST Test Apparatus to estimate the magnitude of the structural deformation in the 30,000-L (8,000-gal) steel and fiberglass tanks. The experiments were designed to measure the important model parameters. Experimental estimates of T, T_{eff}, K, and A_{eff} were made at many levels in the fill tube and in an above-grade standpipe in both the steel and fiberglass tanks.

EXPERIMENTS

All of the experiments were conducted similarly. The tank was overfilled to a level within the fill tube and was allowed to stabilize over a 24-h period before an experiment was started. The waiting period was designed to meet the model assumption that $h(t) = 0$ for $t < t_o$ or $t < 0$. To initiate a test, a bar of known volume was was inserted into the product to instantaneously raise the product level. The product-level and product-temperature changes were measured over a 6- to 10-h period. The bar was then removed and the product-level and temperature data were collected over the next 6 to 10 h.

A_{eff} was estimated experimentally from the volume, ΔV_p, of the bar used to raise the product level in the tank to initate an experiment and from the product level change, Δh, that actually occurred. In many instances, A_{eff} was also measured at the end of the nominal 6- to 10-h tests by repeatedly inserting and removing a bar every 90 s. Values of T_{eff} and K were estimated by fitting the exponential model described by Eq. (9) to the measured product-level time series using least-squares techniques. T was calculated from Eq. (10) once T_{eff}, K, and A_{eff} had been estimated.

Product-level measurements were made using a pressure sensor located at the bottom of the tank. The average rate of change of temperature of the product in the tank was estimated by volumetrically weighting 11 submerged thermistors, spaced vertically at 20-cm (8-in.) intervals.

ANALYSIS

An experiment was conducted in the steel tank on 3 May 1988 to estimate K, T, T_{eff}, and A_{eff}. These data were selected for analysis because the thermally induced volume changes, less than 0.03 L/h, as well as all other product volume changes, were small enough to be negligible. The product-level changes in a 10-cm (4-in.) diameter fill tube were converted to product-volume changes using the measured $A_{eff} = 132.7\ cm^2$. A 5.045-L bar (8.9 cm (3.5 in.) in diameter and 81 cm (32 in.) long) was inserted in and removed from the fill tube of the tank every 6 h over a 12-h period. The rise and drop in the product level was approximately 38 cm (15 in.), only 59% of the expected 64-cm change the initial product level in the fill tube, before the start of the tests, was 30 cm above the top of the tank. The product-volume data were detrended, and the model described by Eq. (9) was fit to the data using a least-squares technique. The results are given in Table 2 and Figure 3.

TABLE 2. ESTIMATES OF A_{eff}, T, T_{eff}, AND K MADE FROM THE PRODUCT-LEVEL MEASUREMENTS IN THE 10-cm (4-in.) DIAMETER FILL TUBE OF THE STEEL AND FIBERGLASS TANKS AT THE UST TEST APPARATUS

Tank	A_{eff} (cm^2)	T (h)	T_{eff} (h)	K (cm^2)
Steel	132.7	3.0	1.6	117
Fiberglass	125.1	2.6	1.6	75

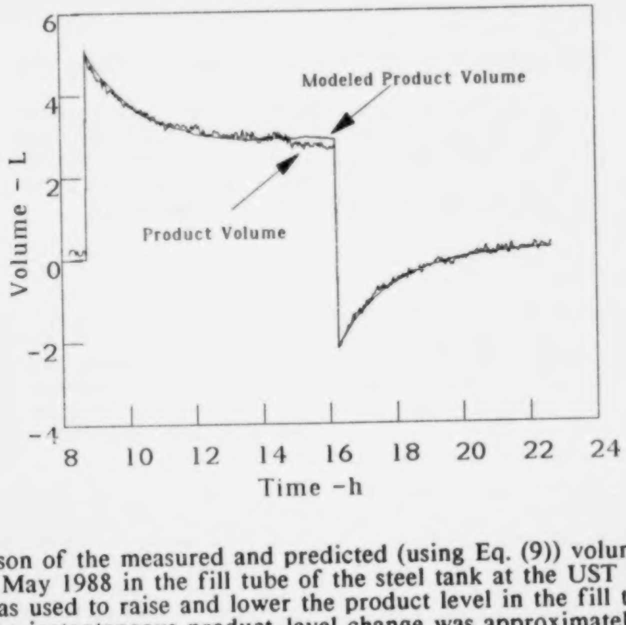


Figure 3. Comparison of the measured and predicted (using Eq. (9)) volume time series for data collected on 3 May 1988 in the fill tube of the steel tank at the UST Test Apparatus. A 5.045-L cylinder was used to raise and lower the product level in the fill tube instantaneously. The instantaneous product-level change was approximately 38 cm, only 59% of the expected 64-cm change.

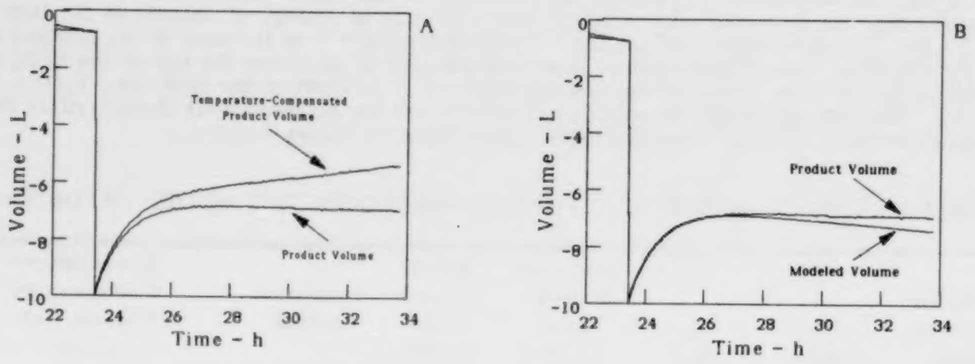


Figure 4. Comparison of the measured and predicted (using Eq. (16)) volume time series for data collected on 10 July 1988 in the fill tube of the fiberglass tank at the UST Test Apparatus. The model includes the thermal contraction of the product in the tank. A 9.460-L cylinder was removed from the fill tube to lower the product level instantaneously. The instantaneous product-level change was approximately 76 cm, only 65% of the expected 117 cm change. The initial product level in the tank was approximately 137 cm (53.8 in.) above the top of the tank.

The results of an experiment conducted in the 10-cm (4-in.) diameter fill tube of the fiberglass tank on 10 July 1988 are shown in Figure 4. A 9.460-L cylinder was removed from the fill tube, causing the product level to drop 75.6 cm (29.8 in.). The initial product level, approximately 137 cm above the top of the tank, exhibited a residual trend from the previous deformation test in which the product level was raised 75.7 cm (29.8 in.) to 137 cm. The product-volume changes, estimated using the measured $A_{eff} = 125.1$ cm², and the temperature-compensated volume change, estimated by subtracting the thermal volume changes (approximately a linear decrease of 0.14 L/h over the entire test) from the measured volume changes, are shown in Figure 4A. Clearly, the temperature-compensated volume rate is not zero after the exponential change in volume due to the deformation has occurred, as expected for a nonleaking tank. The model described by Eq. (16), using the long-term height-to-volume calibration factor, $(A_{eff} + K)$, was fit to the data, and is shown in Figure 4B. The model estimate includes the thermal effects. The agreement between the model and the data is within the uncertainty of the residual trend produced by the previous deformation test. The values of T, T_{eff}, A_{eff}, and K determined are also summarized in Table 2. This suggests that an understanding of the tank deformation effects is necessary in order to make accurate estimates of product-volume changes in an overfilled-tank test. Furthermore, this example suggests that the standard temperature-compensation analysis algorithm is not valid, and can lead to misinterpretation of the results.

MODEL PREDICTIONS OF PRODUCT-LEVEL CHANGES IN THE FILL TUBE

The Fill-Tube Dynamics Model described by Eq. (16) and Eq. (17) was exercised to illustrate how the the product level changed in the fill tube as a function of T, K, and A_{eff}. The constants used in the analysis cover the range of conditions measured in the steel and fiberglass tank experiments at the UST Test Apparatus.

DEFORMATION PRODUCED BY TOPPING THE TANK

Many overfilled-tank tests require that the tank be topped off before the test is started. This may involve adding tens of gallons of product to the tank to elevate the product into the fill tube and an additional gallon or two to attain a specified level within the fill tube, as may be required to begin a test. In addition, many tests require adjustments of the product level in the fill tube immediately prior to or during a test. While the volume changes are typically small, the resulting change in the hydrostatic pressure head may be large.

Eq. (16) was solved for a range of values of K and A_{eff} to illustrate the product-volume changes that are measured after topping, when the rate of change of volume in the tank is -1.2 L/h. The deformation of the tank was modeled for a 1-m increase in the product level in the fill tube. The initial product level was assumed to be above the top of the tank, and constant for all time before simulating the addition of product to the tank (i.e., $V_p(t) = 0$ for $t < t_o$). The rate of change of volume estimated from the product-level changes after the large exponential changes have stabilized is presented in Tables 3 and 4.

TABLE 3. EFFECT OF THE FILL TUBE DIAMETER ON THE MODEL PREDICTIONS[*]

Effective Diameter (cm)	A_{eff} (cm^2)	T_{eff} (h)	Predicted Volume Rate (L/h)	Actual Volume Rate (L/h)	Predicted: Actual	Temperature-Compensated Volume Rate (L/h)
2.5	5.1	0.04	-0.05	-1.2	0.04	1.15
5.1	20.3	0.14	-0.17	-1.2	0.14	1.03
7.6	45.6	0.28	-0.33	-1.2	0.28	0.87
10.2	81.1	0.40	-0.48	-1.2	0.40	0.72
15.2	182.4	0.60	-0.72	-1.2	0.60	0.48
20.3	324.3	0.73	-0.88	-1.2	0.73	0.32
25.4	506.7	0.81	-0.97	-1.2	0.81	0.23
50.8	2026.8	0.94	-1.13	-1.2	0.94	0.07
76.2	4560.4	0.97	-1.17	-1.2	0.97	0.03

[*] Estimates of how $A_{eff} = A$ (i.e., the fill tube diameter) affects the product-volume changes predicted by Eq. (16) that are produced by a 1-m product-level rise resulting from topping the tank immediately before starting a test, and by a -1.2-L/h volume change resulting either from a leak or from thermal contraction of the product. The volume change and the temperature-compensated volume change were estimated after the exponential decay had become small. The predictions were made for K = 120 cm^2 and T = 1 h.

TABLE 4. EFFECT OF TANK ELASTICITY ON THE MODEL PREDICTIONS[*]

K (cm^2)	T_{eff} (L/h)	Predicted Volume Rate (L/h)	Actual Volume Rate (L/h)	Predicted: Actual	Temperature-Compensated Volume Rate (L/h)
0	1.00	-1.20	-1.2	1.00	0.00
15	0.84	-1.01	-1.2	0.84	0.19
30	0.73	-0.88	-1.2	0.73	0.32
60	0.57	-0.69	-1.2	0.57	0.51
90	0.47	-0.57	-1.2	0.47	0.63
120	0.40	-0.48	-1.2	0.40	0.72

[*] Estimates of how K affects the product-volume changes in a 10-cm (4-in.) diameter fill tube. The predictions were made for A_{eff} = 81 cm^2 and T = 1 h.

Tables 3 and 4 show that, as A_{eff} increases and K decreases, more accurate estimates of the actual rate of change of volume can be made. Because only the linear product-level changes (observed after several time constants, T_{eff}, have elapsed) are being analyzed (e.g., see Figure 2), the results are independent of the time constant, T. A longer time constant would require a longer test. The results can be interpreted as either a measurement of a leak in the tank when all other volume changes are negligible, or an estimate of the temperature-compensated volume rate in a nonleaking tank. In the first case, the actual leak rate should be -1.2 L/h, and in the second case, the temperature-compensated volume rate should be 0 L/h.

PRODUCT-LEVEL CHANGES THAT OCCUR DURING RELEVELING

The negative of the cumulative product-volume changes predicted by Eq. (17) for a volume rate, C, are nearly identical to those predicted by Eq. (16) when the cross-sectional area of the fill tube used to estimate product-level changes with Eq. (16) is large enough to approximate a partially filled tank (e.g., $A_{eff} = A > 4560\ cm^2$, which is equivalent to a fill-tube diameter greater than 76 cm), and the releveling time interval is close to zero (e.g., $\lambda < 5$ min). An estimate of the time constant of the cumulative volume time series generated by adding the volume changes predicted by Eq. (17), as a function of the periodic releveling interval, λ, is presented in Table 5. The calculations were made for $K = 120\ cm^2$, $A_{eff} = 125\ cm^2$, $T = 1$ h, and $C = 0$ L/h. The time constant was estimated at the point at which 63% of the total product volume change had occurred. Two points are noteworthy. First, the rate of change of volume approaches the leak rate after the initial exponential deformation has occurred. Thus, accurate tests can be conducted if the waiting period is sufficient for the deformation effects to subside. Second, the time constant is equal to the time constant of the tank, T, when the product is releveled continuously, and increases if releveling is done at discrete intervals. The increase in the time constant, T, as a function of the releveling interval is given in Table 5.

TABLE 5. TIME CONSTANT OF THE VOLUME TIME SERIES*

Releveling Interval (min)	Time Constant (h)
0	1.00
5	1.04
15	1.14
30	1.33
60	1.79

* The time constant was predicted using Eq. (17) as a function of periodic releveling interval, λ. The estimate was made using $K = 120\ cm^2$, $A_{eff} = 125\ cm^2$, $T = 1$ h, and $C = 0$ L/h.

SUMMARY

The Fill-Tube Dynamics Model suggests that the rate of change of volume estimated from the measured product-level changes in an overfilled tank is in error, even if the measurement is made after the large changes initially produced by an addition of product to the tank have stabilized, and even if a measured height-to-volume calibration factor is used. The model calculations illustrate how T, K, and A_{eff} affect the estimate of product-volume changes in the fill tube. Large errors can be made in estimating the product-volume changes produced by a leak rate, or a temperature-compensated volume rate if K is large or A_{eff} is small. The error can be minimized if K is small, A_{eff} is large, or the product in the fill tube is continuously releveled. Increasing the diameter of the container used to measure product-level changes and periodically releveling the product in the fill tube are two methods that can be operationally implemented to conduct accurate tests. In both cases, a waiting period must be included in the test protocol to allow for the effects of tank deformation to become negligible.

The data collected at the UST Test Apparatus also suggest that K is small 1 m above grade, but the data from one set of tanks are insufficient to conclude that conducting a test while product level is well above grade will eliminate the problem.

CONCLUSIONS AND RECOMMENDATIONS

Unless K is known, it is impossible to accurately estimate, from product-level measurements, the rate of change of volume in the fill tube or standpipe during an overfilled-tank test. The theoretical and experimental analyses indicate that all volume changes are coupled in a complicated feedback mechanism. A model of this feedback mechanism has been developed and validated using data collected at the UST Test Apparatus. All volume changes estimated from product-level changes are less than the actual value of such changes if the product-level measurements are made after the exponential change has decayed to a linear change; these estimated changes can be significantly in error. The smaller the fill-tube cross section, the larger the error. If K is small, then accurate tests can be conducted. Since K is not typically known in the field, this commonly used method of testing can result in large errors.

The theoretical and experimental analyses suggest three methods of minimizing or eliminating this error. The most practical is to maintain a constant product level during the test. While this does not eliminate the need to wait out the volume changes produced by the structural deformation of the tank, accurate estimates of product volume can be made by either measuring the volume of product added or removed to maintain the constant level, or by measuring the product-level changes required to maintain the constant level, and multiplying by A_{eff} to convert to volume.

The other two alternatives are less accurate. The measurements on both tanks at EPA's HWERL UST Test Apparatus suggested that K became small when the tests were conducted while product level was well above grade. Also, tests conducted at different times of the year showed that the value of K changed. A test which is designed to take advantage of a small K (e.g., above-grade measurements) can be subject to serious errors if K does not happen to be small for a particular tank system. The theoretical analysis also suggested the fill-tube dynamics can be minimized by increasing A_{eff}. It is possible to increase the product surface area by making the measurements in a larger container located above grade. However, this solution requires more precise product-level instrumentation than is normally used to test an overfilled tank, and the error introduced by evaporation and condensation may be large.

References

1. Maresca, J.W., Jr., J.W. Starr, and R.D. Roach, et al. Evaluation of Volumetric Methods for Detection of Leaks in Underground Storage Tanks Containing Petroleum Fuels. EPA Work Assignment No. 0-1, Research for Abatement of Leaks from Underground Storage Tanks Containing Hazardous Substances, Contract No. 68-03-3409, in preparation.

CASE HISTORIES OF UNDERGROUND STORAGE TANK CORRECTIVE ACTIONS

by: Robert W. Hillger and Richard A. Griffiths
Releases Control Branch
Hazardous Waste Engineering Research Laboratory
U.S. Environmental Protection Agency
Edison, New Jersey

William M. Kaschak and Joyce K. Hargrove
CDM Federal Programs Corporation
Fairfax, Virginia

ABSTRACT

The Environmental Protection Agency's (EPA) proposed regulations for underground storage tanks (UST) require that corrective action be taken in response to a leaking UST. However, the experience of personnel in the EPA regions, the states, and the local environmental agencies in this new field varies widely. As a result, what constitutes appropriate corrective action for leaking underground storage tanks is not well defined. The EPA is expanding its Case History File (File) database on emergency and remedial response actions to include information on UST corrective actions. The expanded database will facilitate technology transfer among the personnel involved in this emerging field of UST corrective action and those involved in hazardous waste site cleanup. This file is a component of EPA's Computerized On-Line Information System (COLIS) which is operated and maintained by the Environmental Emergency Response Unit-Technical Information Exchange (EERU-TIX) contractor, Enviresponse, Inc., at EPA's Edison, New Jersey facility.

The File contains reports filed by On-Scene Coordinators (OSCs) and Remedial Project Managers (RPMs) about technical, administrative, financial, institutional, and other aspects of a spill and/or waste site cleanups they have managed. The File consists of a database section, which allows computerized searches to be made, and a narrative section, which contains detailed reports on the responses. The database section offers menu-driven searches in any of 27 categories. The narrative section is organized into 10 subsections: General Information, Chemical Information, Effects of the Incident, Site Characteristics, Containment Actions, Removal/Cleanup Actions, Treatment Actions, Disposal Actions, Operational Considerations, and Termination of the Response.

The File is being modified to incorporate additional data relevant to UST, such as methods of detection, causes of the UST leak, tank/piping construction, etc. New reports are being added as the EPA receives them from the states and regions. This paper describes the File, the initial UST data collection efforts, and an analysis of the initial data. Synopses of several case histories are presented.

INTRODUCTION

The Environmental Protection Agency (EPA) is planning regulations that will require corrective action for leaking underground storage tanks (UST). However, the experience among EPA, state, and local response personnel varies considerably in this new field; and what constitutes appropriate corrective action is not clear. To clarify this matter and to improve technology transfer among response personnel, the EPA is expanding its Case History File (File) database for hazardous material spills and waste site remedial actions to include information on UST corrective actions. The File is a component of EPA's computerized On-Line Information System (COLIS). It is maintained by the Environmental Emergency Response Unit-Technical Information Exchange (EERU-TIX) contractor, Enviresponse, Inc., at EPA's Edison, New Jersey facility. This group established the original database using files of after-action report forms submitted by On-Scene Coordinators (OSCs) and Remedial Project Managers (RPMs). Several databases were established in accordance with quality control procedures to assure accuracy and reliability. Records are maintained and questions regarding the data may be answered by contacting the System Operator in TIX.

The system has experienced tremendous growth and development since the initial program was installed. Over time, the program has been refined, enhanced, and thoroughly tested to ensure a viable system. The idea of computerizing information retrieval, beginning as the File, has recently been expanded and renamed the TIX On-Line Information System. It will include the original File, with the addition of the UST data, the Countermeasure Selection System, and the Library Search System. Documentation, in the form of a tutorial user's guide, will be distributed and updated as each system becomes available.

The File is an on-line computerized system with a database section and a narrative section: The database section allows searches to be made using any combination of 27 different criteria, such as EPA Region, state, hazardous substance, hydrology, tank/pipe material, corrective action technologies, etc. to quickly identify the case histories of particular interest. The narrative section of the File contains detailed reports in a plain-text format. The narrative section is organized into 10 subsections:

- General Information,
- Chemical Information,
- Effects of the Incident,
- Site Characteristics,
- Containment Actions,
- Removal/Cleanup Actions,
- Treatment Actions,
- Disposal Actions,
- Operational Considerations, and
- Termination of Response.

The intent of the File is to facilitate technology transfer among response personnel who need to select site-specific corrective actions. Most of the data in the database and the narrative sections have been obtained from after-action reports submitted by OSCs or RPMs. The File enables response personnel and planners to examine reports filed by those who faced similar field problems and therefore, benefit from prior successes and discoveries. In turn, the reviewer is prompted to complete after-action reports to pass on their own successes and problems. The File will allow the review of decisions on selecting cost-effective corrective actions on the basis of past performance, cost, practicality, reliability, and other factors. In addition, the File provides the academic and research communities with actual site information, which is essential to developing new and innovative corrective action technologies.

THE ORIGINAL CASE HISTORY FILE

The File is a part of a larger computerized database system, COLIS, that can be accessed remotely using a microcomputer with a modem and telecommunications software. The File consists of numerous small programs and databases. The original databases contained information in the 22 categories shown in Table 1.

TABLE 1. THE ORIGINAL DATA CATEGORIES OF THE CASE HISTORY FILE

1 - Incident Number
2 - Date of Incident
3 - Type of Incident
4 - EPA Region
5 - State
6 - NPL Number
7 - Site Name
8 - Chemicals
9 - Quantity
10 - Origin of Incident
11 - Main Effects
12 - Resources Affected
13 - Area Affected
14 - Population Affected
15 - Geography
16 - Hydrology
17 - Ground Materials
18 - Site Uses
19 - Containment
20 - Removal/Cleanup
21 - Site Treatment
22 - Disposal

The programs display the 22 categories as a menu, and the user selects a category to use for searching. Another program then displays a submenu that contains a list of descriptors (keywords) specific to that category, and the user must select a descriptor to use as the search criterion. The user may conduct up to 10 successive searches, each using different categories or different descriptors within the same category. The results of the searches may then be combined using "and/or" logic to narrow down the selection to individual "incidents".

When the searching is done, the user may examine an abstract for each "incident" identified. The abstract is a one-page summary of the data (in all 22 categories) for an incident. If the summary data shown in the abstract suggest that the incident may be of direct interest to the searcher, a detailed narrative description of the incident may be called up. The content of the narrative varies widely depending upon the type of incident reported and the information available about the incident.

Regardless of length, the narrative section is organized into the 10 subsections shown in Figure 1, which will appear on the screen. The contents of each subsection of the narrative are described in greater detail in MODIFICATIONS OF THE FILE, below.

Subsection	Contents
1	General Information
2	Chemical Information
3	Effects of the Incident
4	Site Characteristics
5	Containment Actions
6	Removal/Cleanup Actions
7	Treatment Actions
8	Disposal Actions
9	Operational Considerations
10	Termination of Response

Figure 1. Screen display of the 10 subsections of the narrative section.

The data is entered into the computer from after-action reports which are patterned after the database and narrative sections of the File. In the brief database section of the report, the OSC or RPM simply circle any descriptors that apply to the incident. In the more lengthy narrative section, a series of questions prompts the OSC/RPM for information relevant to each subsection. Any useful information may be entered.

MODIFICATIONS OF THE FILE

Five new categories have been added to the database section of the File to accommodate information of specific interest to OSCs/RPMs who conduct UST corrective actions:

23 - Date of Report,
24 - Method of Detection,
25 - Depth to Groundwater,
26 - Annual Precipitation, and
27 - UST Construction.

The following provides the rationale used to add new fields to the database.

The date of report establishes the time frame of the report relative to the date of release, corrective action implementation, and promulgation of the regulations. The method of detection was included to capture statistics on the various methods used and to determine any trends as new methods are developed. Depth to groundwater and annual precipitation are two of the many hydrologic/hydrogeologic parameters needed to determine which type of corrective action is likely to be effective for a particular incident. UST construction was included to collect statistical information on materials of construction, backfill characteristics, and any preventive measures initially employed. The above information will assist the OSCs/RPMs in rapidly identifying situations similar to theirs through the search capabilities of the database and, also, limit the number of case histories that they would need to review to obtain beneficial information.

New descriptors also have been added to several of the existing categories. For example, UST corrosion, UST installation error, UST overfill, and UST piping have been added to the origin of incident category. Numerous new descriptors for technologies have been added to the containment, removal, treatment, and disposal categories, as well.

Figure 2 below shows an example abstract of a hypothetical case history as would be seen on the screen of a computer. Note that the new fields are included with the original database fields mentioned earlier. One-or-two word cues are used to identify each field and save space for display of the data. In the event that more data exists than will fit on its appropriate line of the screen, the program will truncate the data (e.g., see Effects in Figure 2). Soil contamination has been truncated to read "soil conta" to avoid overriding CAS #. The data is still in the system.

```
CASE HISTORY FILE                                     Abstract of Incident


Incident : 24                  Type : UST             Inc. date: 12 Mar 87
Region   : 10                  State: WA              Rpt. date: 14 Mar 88
Site name: Big Rob's Service Station                  NPL rank :

Substance: gasoline/benzene                           CAS #    : 71-43-2
Quantity : 200,000 kilograms                          DOT #    : 1114

Origin   : UST corrosion                              Detection: smell
Effects  : human health, fish kill, soil conta        Area     :
Resources: river, pond                                Popula   :
UST const: steel

Geography: other                                      Precip   : 30 in.
Hydrology: confined aquifer                           GW depth : 100 ft.
Ground   : sand, silt, clay
Site uses: commercial, residential

Containmt: trench
Removal  : pump/vac truck
Treatment: thermal destruction
Disposal : recycling, incineration, encapsulation
```

Figure 2. Screen display of an example abstract of incident for the Case History File.

The headings of the narrative subsections have not been altered; however, the information requested in the after-action report has been modified extensively to solicit more UST-related data from the reporter. The modifications to the after-action report are described under THE NEW AFTER-ACTION REPORT, below.

THE NEW AFTER-ACTION REPORT

The after-action report has also been modified to solicit information of specific interest to OSCs/RPMs for UST corrective actions. In addition, the terminology has been changed slightly to accommodate the jargon of the UST industry and the proposed UST regulations. The modifications to the narrative section can be grouped in three major categories: (1) site characterization and assessment; (2) corrective action technologies; and (3) implementation and cost information.

(1) Site characterization and assessment include the subsections on general information, chemical information, effects of the incident, and site characteristics. The general information section was expanded to obtain site history information on the UST facility and the tanks, the nature of the release, and leak detection activities. To capture information on the extent of contamination, the chemical information subsection requests data on the contaminants such as average and maximum product concentrations, and sampling locations for both soil and groundwater. The effects subsection was amended to assess the immediate threat due to the release, such as the potential for fire or explosion, the impact on public health and the environment, and the involvement of emergency service organizations. The site characteristics subsection was expanded to collect information on hydrogeologic studies, site investigation techniques used such as soil gas surveys, lessons learned, and if a risk assessment was conducted. The above information is intended to provide the OSCs and response personnel with information on site characterization techniques and enough information on the site to establish the framework for assessing alternative corrective technologies that may be implemented at the site.

(2) UST corrective action technologies are classified into three separate subsections: immediate, long-term, and free product removal. The immediate corrective action subsection focused on the removal and replacement or repair of the tanks/piping, treatment and disposal of backfill material, and any unconventional/innovative approaches taken. The subsection on long-term corrective actions focuses on the identification and implementation of cleanup objectives and the overall effectiveness of the action upon its completion. The free product removal subsection requests information on collection and removal methods, disposition of recovered product, alternatives that were considered, and any lessons learned. This information provides OSCs who respond to future UST releases with insight on the various methods and techniques employed in carrying out corrective actions.

(3) Implementation and cost information is contained in the subsections addressing effectiveness of the corrective action, operational considerations, and termination of response. The effectiveness subsection

was tailored to specific information on cleanup requirements, termination criteria, and post-monitoring activities. In view of the complexities that may be encountered during cleanup at an UST site, the operational considerations subsection was modified to address technical expertise or support that may have been obtained from outside sources such as federal, state, local personnel, and responsible party consultant, or contractors. In addition, the cost information presented in this subsection is restructured to identify both capital and operational costs for each phase of the corrective action: immediate action, long-term actions for soil, long-term actions for groundwater, and free product removal.

Table 2 synopsizes the salient information requested in the respective narrative subsections.

The after-action report was field-tested and critiqued by several OSCs for UST corrective actions to ensure that the information requested would be available as well as beneficial to response personnel. The OSCs reviewed each element of the database and narrative sections for their potential relevance and use by other OSCs. In a few cases, they recommended including information that was not already specified in the after-action report as either additional fields or field descriptors. The modifications made as a result of the field visits with the state OSCs provided valuable insight in responding to releases from leaking USTS.

DATA COLLECTION

Data collection began with the 10 EPA regional UST coordinators. The EPA UST coordinators indicated that the detailed information on UST sites was located at both state and local offices and recommended states in which to begin our collection efforts. The EPA UST coordinators provided the names and telephone numbers of the state personnel. Checklists were sent to as many state contacts as possible within the available time.

The checklist was developed to collect initial information on sites as a screening tool to reduce the number of sites for the initial data collection effort to a manageable number. The checklist was tailored to ensure that sites selected initially would provide a good representation of diverse hydrogeological conditions, environmental settings, land use activities, and geographical areas. The checklist contains information on tank locations, tank size, quantities and durations of leaks, types of product, hydrogeological data, corrective action technologies used, and cleanup target levels. In addition, the sites were limited to those involving petroleum products.

The checklists were reviewed, and sites were selected for possible inclusion in the case history database. Sites that had completed corrective actions were preferred; however, completed corrective actions involving groundwater are rare. Therefore, the criteria was relaxed slightly to ensure that some groundwater cleanup activities were included. Sites with corrective actions of sufficient duration to evaluate their effectiveness were also considered for inclusion in the database.

The OSC for each selected site was then contacted to determine whether

TABLE 2. CONTENTS OF THE CASE HISTORY DATABASE NARRATIVE SECTION

SUBSECTION HEADING and CONTENT of SUBSECTION

General Information:
    Contact information, tank information, leak detection, verification methods, and extent of leak

Chemical Information:
    Primary substance involved in the leak, initial concentration, Sampling location, test method, and hazards encountered

Effects of the Incident:
    Effects on public health and the environment, anticipated impact if no action was taken

Site Characteristics:
    Land use, hydrogeologic study, geology of site, data quality objectives, site characterization techniques used, indicator compounds, and risk assessments

Containment Actions: (Immediate corrective action)
    Selection rationale, effectiveness, duration, tank/piping removal, protocols, problems, innovative approaches, and disposal methods

Cleanup/Removal Actions: (Long-term corrective action)
    Selection rationale, effectiveness, duration, cleanup level requirements, and problems encountered

Treatment Actions: (Free product removal)
    Selection rationale, effectiveness, duration, fate of recovered product, fate of contaminated water, and any problems encountered

Disposal Actions: (Effectiveness of corrective actions)
    End point concentrations, termination criteria, post-monitoring period

Operational Considerations:
    Required permits, contacts providing technical advice/support, public involvement, administration problems, and cost information

Termination of Response:
    Cleanup assessment, and any additional comments

they preferred to: complete an after-action report themselves; provide copies of other reports and files so that our project team could complete an after-action report; or have the project team visit their office to complete the report. Whenever possible, site visits were arranged in order to observe the corrective action in progress.

After-action reports were sent to 24 states and the District of Columbia. Individuals who agreed to a site visit were sent after-action reports in advance to familiarize them with the information required.

The states that participated in the initial data collection efforts, the information they provided, and the locations of site visits are shown in Figure 3. Fourteen states and the District of Columbia provided eighty-four checklists. Site visits were made to 14 ongoing corrective actions in 7 states. As of March 21, 1988, 46 after-action reports have been collected from 15 state and 7 local offices. Twenty-nine after-action reports were completed from copies of files; 9 were obtained through site visits; and 8 were completed by OSCs.

PRELIMINARY RESULTS

CORRECTIVE ACTION TECHNOLOGIES

A rigorous evaluation of the corrective action technologies is in progress. A full report on the findings and conclusions of this project is to be released by EPA in July 1988.

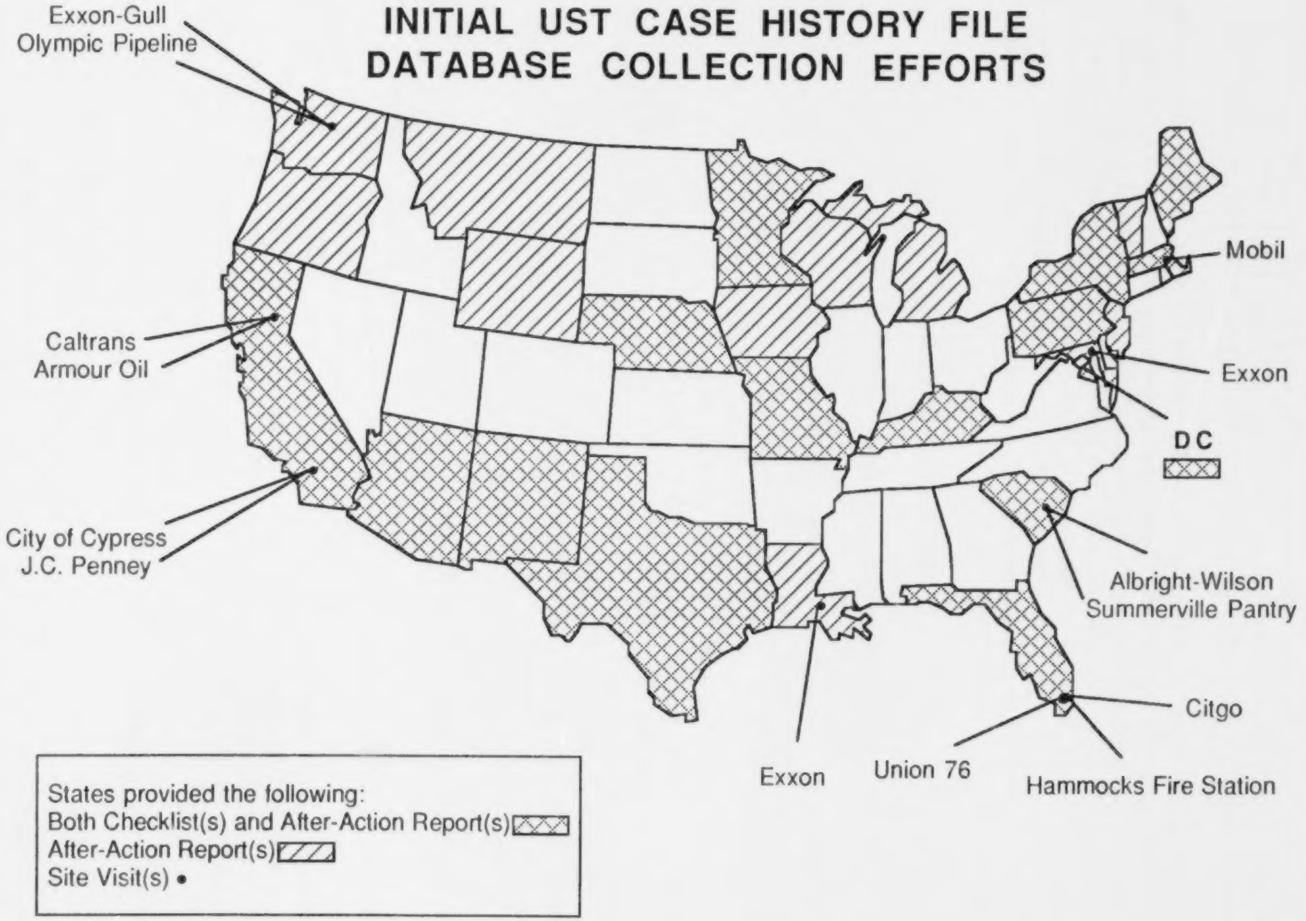
A variety of corrective action technologies are being used in responding to UST corrective actions. Although some technologies may be effective by one aspect of the UST corrective action, typically a combination of technologies is necessary to obtain required cleanup levels in a reasonable period of time. Choice of a technology should be influenced by the extent of contamination, hydrogeological characteristics, topography, environmental sensitivity, duration, cost, and other factors. Still, several technologies are used more often than others.

The following sections discuss the most commonly used corrective action technologies as characterized by the phase of the corrective action in which they were used: immediate response, free product removal, soil remediation, and groundwater remediation. Derived from checklists completed by OSCs/RPMs, the tables presented in each section illustrate the frequency of a technology in a specific phase of the corrective action. Each phase of the corrective action usually consisted of several technologies used in combination. This results in the sum of the frequencies being greater than the number of UST corrective actions identified (N).

Immediate Response

Immediate response actions are initial corrective actions taken to mitigate the impact of a sudden or newly detected release and are usually taken within hours of the release being discovered. These actions focus on source control and collection and containment of the released product so as

FIGURE 3
INITIAL UST CASE HISTORY FILE DATABASE COLLECTION EFFORTS


Exxon-Gull
Olympic Pipeline
Caltrans
Armour Oil
City of Cypress
J.C. Penney
Mobil
Exxon
DC ▩
Albright-Wilson
Summerville Pantry
Citgo
Hammocks Fire Station
Union 76
Exxon
States provided the following:
Both Checklist(s) and After-Action Report(s) ▩
After-Action Report(s) ▨
Site Visit(s) ●

to minimize immediate risks to human health and the environment. Typical immediate response actions are presented in Table 3. Of the 77 sites surveyed that initiated immediate responses, 45 sites had tank removals, 33 sites pumped out free product, 30 removed the piping and fittings, 28 sites excavated contaminated backfill, and 18 sites repaired the pipe system. Some of these actions were conducted as sole efforts while some sites conducted a series of these response actions. Each of these is a practical and reliable method of source control. Pumping free product and excavating backfill are also effective means of preventing further contamination. Removing and repairing the pipe system as part of the immediate response reflects the incidence of UST leaks attributable to faulty piping.

TABLE 3. IMMEDIATE RESPONSE ACTIONS CITED IN THE CHECKLISTS

Technology	Frequency (N=77)
Remove Tank	45
Pump Free Product	33
Remove Pipe System	30
Excavate Backfill	28
Repair Pipe System	18
Containerizing	4
Empty Tank	3
Repair Tank	3
Excavation	1
Flush with Water	1
Venting	1

Free Product Removal

Free product removal generally refers to the recovery of product that is located in various subsurface settings in large enough quantities that it can be removed by mechanical methods. The free product may collect on impermeable strata, collect in small subsurface basins, or enter an aquifer where the free product will either float on the water or sink to the bottom depending on the density of the free product. Although usually initiated as part of the immediate response, free product removal may be of extended duration. In either case, free product must first be pumped to the surface where it can then be recycled or discarded.

Free product removal involves creating a water gradient or manipulating an existing one so the product can be collected and subsequently retrieved. Depending on the method used for collection, an additional mechanism is required to separate the product from water. Technologies used to accomplish these tasks are identified in Table 4.

Systems typically used to collect product are pumping wells, which create a cone of depression, and trenches, which intercept the flow of free product. Pumping wells (also known as recovery wells) may have either a dual pump or single pump installed. Dual pump systems separate product and water in the well and are commonly used to maximize petroleum/water separation. In a single pump system, product and water are retrieved together and must be separated aboveground in an oil/water separator. The 10 recovery wells mentioned in Table 4 refer to those cases where recovery wells were installed for free product removal but the associated pump system was not specified.

In situations where the water table is relatively shallow, digging a trench may effectively collect the product. Portable devices capable of separating free product from water include vacuums, sorbant pads and bailers.

TABLE 4. FREE PRODUCT REMOVAL METHODS CITED IN THE CHECKLISTS

Technology	Frequency (N=54)
Vacuum	12
Dual Pump	10
Recovery Well	10
Single Pump	9
Scavenger	7
Oil/Water Separator	5
Skimmer	5
Trench	4
Excavation	2
Sorbent Pads	3
Bailer	2
Separation Tank	2

Soil Treatment

Contaminated soil may be excavated for treatment and/or disposal or treated in situ. Excavation can be completed in a few days or take several months depending on site specific complexities. With treatment techniques, it may take months to years to achieve complete remediation. Table 5 indicates that excavation is commonly used to remove the contaminated soil. However, its applicability is limited to small volumes of soil and shallow excavations. The most commonly used on site technology for soil treatment is ventilation/aeration. Another on site technique that has been implemented to a limited extent, but gaining popularity, is bioremediation. Several cases where these techniques have been successfully applied are included in the database.

TABLE 5. SOIL TREATMENT/DISPOSAL TECHNOLOGIES CITED IN THE CHECKLISTS.

Technology	Frequency (N=46)
Excavation	17
Ventilation/Aeration	16
Bioremediation	8
Thermal Destruction	2
Vacuum Wells	1
Soil Scrub	1
Solidification	1
Natural Attenuation	1
pH Adjustment	1

Groundwater Treatment

Although corrective actions for groundwater may entail treatment, containment or dilution techniques, the results of the project indicate that treatment technologies tend to prevail. Remedial methods commonly employed are summarized in Table 6. Airstripping, carbon adsorption and bioremediation were applied in 76% of the corrective actions requiring groundwater remediation. Air stripping was encountered at 28 out of 55 sites conducting groundwater remediation. The ease of operation, high removal efficiency, and relatively low cost account for its popularity. Air stripping is often followed by carbon adsorption treatment as a polishing step to achieve maximum clean-up levels. In situations where the influent organic concentration is not excessive, carbon adsorption has been used independently of air stripping as the sole treatment technique. Bioremediation utilizes microorganisms to restore contaminated groundwater. This may be accomplished by (1) adding nutrients and/or oxygen to the aquifer to enhance the growth and activity of indigeneous microorganisms; or (2) by injecting the aquifer with genetically engineered microorganisms. Bioremediation, which may be a cost effective and efficient treatment technique for contaminated groundwater, is gaining stature as a viable alternative technology.

TABLE 6. GROUNDWATER TREATMENT TECHNOLOGIES CITED IN THE CHECKLISTS

Technology	Frequency (N=55)
Air Stripping	28
Carbon Adsorption	15
Bioremediation	7
Divert to Sewer	7
Oil/Water Separator	6
Natural Flushing	2
Trench	2
Containerizing	1

SUMMARY

The Case History File contains reports on both surface spills and UST leaks. A database section permits computerized searches on 27 key categories relevant to hazardous materials releases, and a narrative section that accommodates more detailed information on site characterization and assessment, corrective action technologies, and implementation and cost information. Regional, state, and local level agencies contributed case histories to the file and data collection efforts are still in progress.

A variety of reliable technologies are available for UST corrective actions. Those technologies used most frequently have been established as cost effective, dependable, efficient, and relatively easy to implement. Some of these technologies may, in fact, lend themselves to a broad spectrum of sites and circumstances. Since there is always room for improvement, the industry needs to acquire a better understanding of existing technologies as well as develop innovative and alternative technologies.

ACKNOWLEDGEMENT

We would like to acknowledge the contributions of May Smith of Enviresponse, Inc. and the staff of the Technical Information Exchange in the development of the Computerized On-Line Information System (COLIS) and the original Case History File. The assistance of Rachel Simmons with data management and documentation is gratefully acknowledged. The authors also acknowledge the support provided by Mr. James Begley of the Massachusetts Department of Environmental Quality Engineering and Mr. Phillip Cole of the New Jersey Department of Environmental Protection for their professional assistance in critiquing the initial draft of the Case History File After-Action Report for UST.

DUST AND VAPOR SUPPRESSION TECHNOLOGIES FOR USE DURING THE EXCAVATION OF CONTAMINATED SOILS, SLUDGES OR SEDIMENTS

by: Quintin R. Todd, William Beers,
William Celenza, Peter Puglionesi
Roy F. Weston, Inc.
EPA-OHMSETT Facility
Leonardo, New Jersey 07737

ABSTRACT

Currently available dust and vapor suppression technologies for use during the excavation of contaminated soil, sludges, and sediments were surveyed. Several types of commercially available suppression technologies were identified for utilization by on-scene coordinators, cleanup contractors, and design engineers. Each technology is described and reviewed for its applicability, effectiveness, implementability, cost, and relative advantages and disadvantages. Application guidelines and selected case studies are also discussed.

INTRODUCTION

As the number of Superfund sites undergoing remediation increase, there is a growing need for dust and vapor suppression measures at the job site during remediation activities such as soil loading, unloading, and transport prior to treatment or disposal of hazardous material. Although personnel protective equipment has been used successfully to mitigate adverse on-site exposure to dust and vapor, this measure cannot typically be extended to mitigate potential adverse off-site exposures.

Site remediation activities historically have included the excavation, loading, transportation, and unloading of hazardous materials, and the need for dust and vapor control technologies beyond conventional construction dust control measures has been recognized recently to be of growing importance. As a result, research, commercial development and application of new control technologies are in an early and active phase. This study was commissioned to provide a current update on the state-of-the-art and to provide the individual assigned to design the remedial program with current information on availability and application. As a logical outgrowth of the study, areas where further research is necessary to develop technologies and/or to provide objective and accurate performance data were also identified.

APPROACH

One of the first steps in conducting the study was to identify the types of materials, pollutants, unit operations, and environments that would confront the typical remedial program designers in their efforts to develop dust and vapor control plans for Superfund sites. A review of existing EPA Record of Decision (ROD) files for Superfund sites provided representative information. This served as a basis for characterizing future dust/vapor control requirements and also provided information on which technologies are currently in use.

In parallel with this effort, information on conventional and newly available technologies was obtained using computer assisted literature searches and personal contacts with U.S. EPA personnel, remediation contractors, consultants, and others working in the remediation design/implementation area.

In this paper, each technology is briefly discussed and summary information is provided on how these technologies may be appropriately applied. Two tables were developed summarizing cost data as well as providing brief assessments of applicability and performance. The project report provides additional detail on selection and performance as well as case histories where various dust and vapor suppression technologies have been applied. These case histories provided additional insight in visualizing how the individual suppression techniques can be effectively applied to control the emissions during an active excavation.

TECHNOLOGIES

Thirteen categories of commercially available dust and vapor suppression technologies were identified. These are briefly described as follows:

1. Water - The addition of water to soils and excavations needing dust control continues to be one of the most common suppression techniques for dust and chemically contaminated dust particles. Water is applied topically to increase the density and cohesion of soils, thus preventing release to the atmosphere. Repeat applications are necessary due to evaporative losses. The effectiveness of many of the other control techniques for dust is frequently related to that for water alone as a standard for reference because it is the most well-established dust control technology.

2. Water Additives - Water additives are typically surfactants and other water extenders that increase the penetration and staying power of topical applications in order to reduce the frequency of application and the attendant labor costs relative to waste alone. Adhesive type polymers such as latexes, acrylics, and the waste-derived lignosulfonates are typical examples of this class of dust suppressant. Numerous commercial formulations are available.

3. Inorganics - Hygroscopic inorganic salts such as calcium chloride have long been used to control dust on unpaved roads. These salts absorb and

chemically bind moisture. When integrated into a roadway with the proper soil particle size distribution, the salt retains moisture over a long period of time and reduces the release of dust to the atmosphere. Alternatively, pozzolanic material such as cement and lime can be incorporated into the soil. These pozzolans react with water to provide higher soil cohesion and strength, thus reducing the release of dust.

4. Organics - Oils, waste oils, bitumens, and vegetable gums have historically been used to wet and bind particles together to resist entrainment by blowing winds and drafts created by earth moving equipment. These materials have an affinity for soils and a lower vapor pressure than water, and thus remain effective longer than water.

5. Foams - Vapor and dust suppression has been demonstrated by foams which are produced by air entraping water additives. This relatively new technology was originally developed for fire fighting and several available products are modifications of fire fighting foams. Blankets of these foam products suppress the evolution of particles and vapors by physically blocking escape routes and insulating the soil from the effects of the sun and wind. Stabilizers are commercially available to extend the life of these foams to several days. Specialized nozzles or conventional fire fighting foam producing nozzles are used depending on the commercial formulation.

6. Air-Supported Structures - Commercially available air supported membranes have been applied to enclose areas undergoing excavation. The membrane provides a barrier which prevents uncontrolled release to the atmosphere. In conjunction with air lock entrances and exhaust stream dust and vapor pollution control equipment, these structures have the capability for relatively high effectiveness where site conditions permit their use.

7. Acid Gas Neutralization Additives - Drilling technologies adapted from the nature gas and oil industry have been used with some success in working with contaminated soils. Specifically, ferrous compounds used in the drilling mud have proven effective in reacting with and retaining sulfurous gases below the surface in the bore hole. While it has not been commercially applied to soil excavation, such solutions may be applied topically during excavation.

8. In Situ Treatment - Several technologies are available for in situ treatment of volatile organic compounds which could be applied to remove vapors prior to, or in lieu of, excavation. These include in situ volatilization, biodegradation, soil flushing, and steam stripping.

9. Self-Supporting Enclosures - A variety of relatively inexpensive enclosures have potential application for containing dust and vapor during excavations. These can provide a barrier to release of contaminants from the work area. Unlike air supported structures, the building can be operated at or slightly below atmospheric pressure for the purpose of directing purge air to air pollution control devices. Dual radius arch frames supporting corrugated steel or textile covers,

geodesic domes, and construction equipment hangers may fined successful application during excavations. One reported application included a moving self-supported structure that advanced on rails along side the excavation as the work proceeded.

10. Vacuum Trucks - Commercially available vacuum trucks with liquid and/or dust separation and control equipment can be used to remove soils and sludges fluid enough to flow to the pickup nozzle. In these cases it can provide a more controlled alternative to excavation and loading. Similarly, paved roads can be swept clean and vacuumed to control dusts.

11. Covers, Mats, Membranes - Various systems are available for covering soil with physical barriers. These include thin (4-6 mil) plastic sheets, thicker (30-40 mil) covers, mats, geotextiles, and bulk materials such as straw, wood chips, and sludges. Some barriers are applied from rolls which are held in place and later removed during excavation. These are only effective for controlling the release of dust and vapors between active soil handling unit operations (i.e., inactive excavation, stockpiling, transport in truck, etc.). Others which are applied in bulk, such as paper mill sludges, straw, aged manure or other adsorbent materials, can be removed for disposal along with the soil.

12. Windscreens - Agricultural engineering practices include the use of windscreens to reduce windshear over soils to control the amount of soil erosion. Similar methods can find use in controlling emissions from excavations and temporary waste storage piles. Design guidelines and effectiveness measurements are currently available in the literature.

13. Seasonal Scheduling - Planning excavations according to the seasons can reduce the overall potential for emissions by taking advantage of lower temperatures and wind speeds, and avoiding excessively dry weather. In addition, monitoring the emissions downwind during remediation activities can also be used to adjust daily work schedules and, if necessary, stop work or apply additional dust or vapor controls as meteorological conditions and observed emission levels vary.

APPLICATIONS

A survey of current practices where dust and vapor emissions were considered a potential problem was performed polling on-scene coordinators or other responsible persons who could relate the experience obtained at the sites of interest. The majority of the roughly 100 sites we surveyed either practiced no overt dust and vapor control or employed some form of natural dispersion to the atmosphere. Water spraying, daily or seasonal scheduling, and covers of various types were the technologies that were the most commonly used. Relatively few sites reported use of chemical additives to enhance water spraying or the enclosure of the remediation in a temporary building or structure. Specifically, 15 sites utilized water spray to control dust and 11 sites utilized covers, mats and membranes for dust or vapor suppression. Four sites utilized chemical suppressants to aid in vapor control. Four sites specifically utilized to control dust.

Additional quantitative performance and cost data are required to justify the use of temporary enclosures or chemical additives. Similarly, additional quantitative estimation of potential emissions based on site conditions may be needed at the planning stage. The survey highlighted the less-established control methods. Foams, for example, do not appear to have been used much in the control of dust and vapor to date.

1. Planning--The remedial program designer must first consider the site conditions, soil/sediment/waste characteristics, and planned remedial activities in order to quantify the potential for dust and vapor emission control problems. The following parameters should be considered when making this estimate:

    1) Distance to nearest residence or other receptors

    2) Relative volatility of the potential vapors

    3) Threshold Limit Value (TLV) or other relevant standards for contaminants of concern

    4) Odor threshold of the potential vapors

    5) Temperature, wind direction and speed, humidity, time of year, and other meteorological parameters prevail during the time of the planned excavation

    6) Particle size distribution and moisture content of the soils and sediments

    7) Square footage of area to be excavated and the planned depth of excavation

Generally, given contaminants of moderate mobility and toxicity at moderate concentrations, the designer could approach the problem by utilizing readily implementable conventional technologies (i.e., water, water additives, organics, inorganics, covers, and seasonal scheduling) in conjunction with site perimeter monitoring for contaminants of concern or representative indicator parameters. If during remedial activities monitoring should detect elevated concentrations of dust and vapor, other, more aggressive, techniques (i.e., foams, windscreens, scheduling in response to meteorological conditions) can be specified as contingency measures.

If contaminants of concern are present at higher concentrations (i.e., waste materials) or have relatively high toxicity and mobility, a more rigorous projection of off-site impacts during remediation may be warranted, if not already completed, in the site assessment or RI/FS work. This may consist of a focused risk assessment including dust/vapor generation and dispersion modeling in conjunction with the identification of appropriate short-term exposure risk action levels. The methodologies available for such assessment are available in the technical literature.

If the assessment indicates that significant off-site exposures could potentially result, more rigorous emission control technologies should be applied, such as planned, programmed use of windscreens and foams or the construction of enclosures which can exert positive control of emissions.

2. Case Studies--Nyanza Chemical, Ashland, Massachusetts, and Bruin Lagoon, Butler County, Pennsylvania, both Superfund Sites, and test work at Cincinnati, Ohio, were three cases selected for further study. Each of these cases had special noteworthy features which should assist the reader in understanding how one of nine of the control technologies would work under specific field conditions.

   NYANZA CHEMICAL, ASHLAND, MASSACHUSETTS, is noteworthy for its use of in inflatable building. An area approximately 80' wide by 105' long was enclosed. The building was leased to save money after a vendor was found who would accept the decontamination procedures. However, unplanned expenses were incurred when it was found to be necessary to bring in a drilling subcontractor to set the anchors for the building even though the vendor has indicated manual installation of the anchors would suffice. Even so, the leased building was less expensive to install and use than comparably sized self-supporting structures. The inflatable building was leased at a rate of $14,000 for four months; a comparable self-supporting structure was estimated at a cost of $120,000. Building permits were required for the inflatable structure even though it was a temporary installation. Ventilation was provided with two blowers controlled by a differential pressure switch which maintained an inside air pressure 3/4" to 1 1/4" above atmospheric pressure. 15,000 CFM fans supplied approximately four to five air changes per hour. An air lock entrance supplied with the building was used to admit and remove earth-moving equipment without significant loss of air pressure. The spent air was filtered through a radial design carbon adsorption unit with a relatively low pressure drop overcome by a separate, dedicated 5-hp fan. Work inside the building was carried out in level B protective gear because of the carbon monoxide levels resulting from operating the earth-moving equipment inside the building. The excavated soils were incinerated on-site to destroy volatile organic compounds and then returned to the ground. The inflatable building assisted this treatment by excluding weather and moisture from the soils to be excavated.

   The main lesson in this case history is that commercially available inflatable buildings can be practical field solutions for sites where excavations need to be enclosed.

   BRUIN LAGOON, BUTLER COUNTY, PENNSYLVANIA, began operations in the 1930's and, for over 40 years, was used as a disposal site for mineral oil production sludges, acidic and oily wastes, coal fines, fly ash, and waste sludges from the reclamation of used motor oil.

   The initially selected remediation consisted of on-site stabilization and containment. A substantial amount of this remedial work was completed when hydrogen sulfide and other related acidic gases were encountered during the remediation work. Analytical results from test borings showed hydrogen sulfide emissions approaching 1,000 ppm by volume in the air.

Modified drilling methods were used to contain and actively vent the trapped acidic vapors to a carbon adsorption train. Ironite drilling mud was utilized to adsorb hydrogen sulfide. A special well head was fabricated to facilitate sampling of the well for water and the air headspace. The cost of the special well requirements were not broken out. The drilling subcontract cost of installing 10 shallow wells, 10 deep wells and 6 soil borings was approximately $150,000.00. In summary, previously stabilized sludge was used to form a cover over the remaining lagoon surfaces, specialized drilling mud and special well head construction were used to penetrate this cover while installing monitor wells which act as vent pipes, and carbon adsorption was used to clean the vented acidic gases.

TEST SITE, CINCINNATI, OHIO. Test work performed at a small farm near Cincinnati, Ohio, was analyzed in detail because of its effort to quantify the effectiveness of conventional dust control measures while using a front-end loader and a dump truck, two earth-moving devices that are commonly used at excavation sites.

Three instrument towers were used, one upwind, one downwind, and one between the excavation site and the dump truck station. These locations allow distinguishing between dust emissions from the active excavation and dust emissions from the dump truck loading operation.

A spray treatment with water and with water and a water extender achieved dust suppression efficiencies of 60 to 70 percent on particles less than 2.5 microns from the excavation itself. Water curtains and foam treatments at the dump truck loading station were less effective and suffered operational problems.

3. Application Guidelines--The applicability of each technology to vapor and dust control problems was evaluated in the study. The advantages, disadvantages, and constraints in applying each technology are summarized in Table 1. Several technologies, (including water additives, inorganics, organics, and foams) require the purchase of raw materials from one of a large number of potential suppliers. These materials are available in numerous formulations and have a wide range of raw costs as well as a wide range of application rates which impact costs. The products identified in this study are listed in Table 2 along with a summary of the available information on final material costs in dollars per acre.

The costs of implementing other vapor suppression technologies were estimated based on material costs and a generic conceptual application to arrive at an installed cost on the basis of dollars per square yard of contaminated surface. These estimated costs were developed solely for comparative purposes. These relative costs are presented in Table 3. In order to assess relative site specific costs on a preliminary basis, the designer must consider what areas and operations will be conducted whether reapplications will be necessary, whether point source air pollution control devices may be necessary, as well as the site-specific cost factors such as regional labor rate differences and the impact of working with Health and Safety equipment.

CONCLUSIONS AND RECOMMENDATIONS

This study provides a broad review of currently available dust and vapor control technologies. The performance of the older conventional control methods for dust appears more firmly understood. However, the performance of the newer vapor suppression technologies such as in situ treatment and foam is much more uncertain at this time.

This uncertainty suggests additional research is needed to support a model allowing the quantification of emissions of different pollutants from different soils during various excavation processing steps with changing weather conditions.

Moreover, while existing atmospheric models and health related ambient air standards may be used to define the downwind concentrations resulting from these estimated emissions, additional research into quantifying the effectiveness of the proposed and newly developed control measures is needed.

Given the cost and time required that will be required to gain this experience, it will be necessary to mobilize and monitor the performance of dust and vapor suppression technologies in the field during removal actions or site remediations while monitoring their performance during use without knowing beforehand what the overall efficiency will be. The costs of collecting and monitoring suitable operational variables during work in the field should be included in the planning stages of the remediation.

In addition, another area of concern and one requiring additional research is the treatment and disposal of any dust and vapor suppressant residuals on a site. The limited data to date indicates the potential for environmental contamination, technology feedstock problems and the formation of additional toxic materials on-site.

TABLE 1. APPLICATIONS GUIDELINES FOR DUST AND VAPOR TECHNOLOGY

Technology	Application In Dust Control	Application In Vapor Control	Constraints In Use	Benefits Of Use
Water	Yes	Low Effectiveness	Runoff Reaction with pollutants Costly repeat applications Time consuming Low effectiveness with vapors	Cost-effective method widely available.
Water Additives	Yes	Low Effectiveness	Reaction with pollutants Limited availability Low effectiveness with vapors	Extended benefits of water by reducing costs of repeated application.
Inorganics	Yes	Low Effectiveness	Reaction with pollutants Effective only on relatively non-disturbed soils Low effectiveness with vapors	Cost-effective method that requires infrequent application.
Organics	Yes	Yes	Specialized applicators Reaction with pollutants Material handling constraints Application temperature Dependent	Effective in dust suppression. May add BTU value to soil. May provide tough dimensionally stable continuous membrane may be used with geotextiles.
Foam	Yes	Yes	Reaction with pollutants Specialized applicators Material handling constraints Relatively short life Some toxic decomposition Products upon heating	Existing marketing towards HW site use overnight vapor suppression. May produce stable blankets. Slow drainage rate. May resist product pickup.
Air-Supported Enclosures	Yes	Yes	Cost may restrict use to smaller sites -- potential greenhouse effect	Available nationwide for lease/purchase no chemicals introduced into system.
Acid BAS Neutralization Additives	Yes	Yes	Reaction with pollutants untested in this application	Demonstrated technology for same contaminants in drilling applications.

TABLE 1. APPLICATIONS GUIDELINES FOR DUST AND VAPOR TECHNOLOGY (continued)

Technology	Application In Dust Control	Application In Vapor Control	Constraints In Use	Benefits Of Use
In Situ Treatment	No	Yes	Effective on highly permeable soil use on limited group of compounds - effectiveness dependent on soil character	Removes vapors before excavation may obviate need for excavation.
Self-Supporting Enclosures	Yes	Yes	Cost may restrict use to small sites Construction may disturb site Potential greenhouse effect	Effective containment of dust and vapor.
Vacuum Trailers	Yes	Yes	Requires control of airborne pollutant Limited to applicable materialso (e.g., sludges, loose granular material)	No additional chemicals used.
Covers, Mats and Membranes	Yes	Yes	Must be removed during active Material handling Mat/liner failure Potential greenhouse effect	Ease of application. Effective control in many situations.
Windscreens	Yes	No	Subject to wind direction Marginally effective	
Scheduling	Yes	Yes	Stockpiles Dependent on weather conditions - rigorous timing constraints	Seasonal scheduling - least costly method. Can be applied on contingency basis.

TABLE 2. REPRESENTATIVE SUMMARY OF DUST AND VAPOR SUPPRESSANT PRODUCTS

Product Type	Typical Material Cost ($/Acre)	Form
Calcium Lignosulfates	60	Organic Binder
Calcium Chloride	230	Inorganic Binder
Sodium Silicate	340	Inorganic Binder
Vinyl Acetate Resins	480	Water Additive
Acrylic Emulsions	500	Water Additive
Ammonium Lignin Sulfates	620	Organic Binder
Asphalt Emulsion	1,100	Organic Binder
Soil Enzyme	1,400	In Situ Injectable
Wood Fibers with Plastic Netting	1,700	Covers, Mats, Membranes
Cellulose Fabric	2,200	Covers, Mats, Membranes
Polyurethane-Polyurea Foam	8,400	Foam
Sodium Bentonite Clay	16,500	Covers, Mats, Membranes
Sodium Bentonite and Geotextile Fabric	26,100	Covers, Mats, Membranes

TABLE 3. APPLICATIONS AND COST GUIDELINES FOR DUST AND VAPOR TECHNOLOGY

Technology	Dust Control Application	Vapor Control Application Effectiveness	Relative Costs
Water	Yes	Low effectiveness	Low
Water Additives	Yes	Low effectiveness	Low
Inorganics	Yes	Low effectiveness	Low
Organics	Yes	Yes	Low - Moderate
Foam	Yes	Yes	High
Air-Supported Enclosures	Yes	Yes	High
Drilling Mud Additives	Yes	Yes	Low - Moderate
In Situ Volatilization	No	Yes	Moderate - High
Geodesic Domes/Semi Permanent Structures	Yes	Yes	High
Vacuum Trailers	Yes	Yes	High
Mats and Liners	Yes	Yes	High
Windscreens	Yes	No	Low - Moderate
Scheduling	Yes	Yes	Very Low

LABORATORY STUDIES OF VACUUM-ASSISTED STEAM STRIPPING OF ORGANIC CONTAMINANTS FROM SOIL

by: Arthur E. Lord, Jr., Robert M. Koerner and Vincent P. Murphy
Geosynthetic Research Institute - Drexel University
Philadelphia, Pennsylvania 19104
and
John E. Brugger
Hazardous Waste Engineering Research Laboratory
U. S. Environmental Protection Agency
Edison, New Jersey 08837

ABSTRACT

A long-term research and demonstration project is underway to investigate vacuum-assisted, steam stripping of organic chemicals from contaminated soil and to develop a field unit to steam strip and collect such pollutants. In this paper, an analytical approach is developed to model steam stripping in the field. The model involves steam flow from pipes embedded below the ground surface. The data needed to use the model are obtained from an experimental effort that includes the following (in a variety of soil types, e.g., sand, silt, clay):

- observations of the transient steam-front movement in two-dimensional flow
- measurements of steam permeability in conventional one-dimensional flow
- measurements of steam stripping efficiency with kerosene as the pollutant.

The analytical model was used with a variety of soil types to predict such parameters as:

- time for the steam front to reach the ground surface
- total steam flow rate through the ground surface into the vacuum-assisted surface collection assembly [the surface is overlaid with a unique construction of geosynthetic (polymeric) material]
- time needed to decontaminate a given sized spill of kerosene.

For a typical spill, the predicted times (and costs) for decontamination via steam stripping appear to be quite reasonable compared to those for other decontamination methods. For final verification of the approach, field studies will be undertaken.

This work was performed under EPA Cooperative Agreement No. CR-813022-01.

INTRODUCTION

Soils can be contaminated by chemical spills (highway or railroad accidents), leaking underground tank releases (gasoline or other), intentional dumping or leaking, etc. It is imperative that such contamination be prevented from reaching the groundwater. Fortunately, in many locations, a partially saturated or vadose zone exists between the groundwater and the ground surface and acts as temporary containment volume and retards the downward movement of the pollutant. The time of containment varies (over large ranges) depending on the effective permeability and absorptivity of the vadose zone soil.

There are a number of options in remediation (i.e., clean up) of the soil. They are:

- Excavation and off-site disposal
- Excavation and on-site treatment
- In-situ treatment via a number of methods, e.g., physical, chemical or biological.

A number of these techniques (and others) have been reviewed in recent articles (Kovalic and Klucsik, 1987 and Cheremisinoff, 1987). There are problems with the excavation techniques, not the least of which are the very high costs and the local residents' very strong aversion to nearby landfilling and incineration. The U. S. E.P.A. has recently instituted the Superfund Innovative Technology Evaluation (SITE) program which is undertaking a number of full scale field evaluations of in-situ remediation methods (Hill, 1987).

IN-SITU REMEDIAL MEASURES

The following in-situ remediation techniques are being used in the field or are being studied at the research and development stage.

AIR STRIPPING

Air is forced through the contaminated soil (via injection and extraction wells) and the volatile contaminants that are not attached too strongly to the soil particles are removed in the air stream. Increased efficiency of removal can be obtained by heating the air. The method is applicable to volatile chemicals in loose permeable soils. The method is described and discussed in Ghassemi (1986) and field studies are described in Anastos (1987).

VAPOR EXTRACTION

This method has a similarity to air stripping but in this case the air plus contaminant is pulled through the soil by an applied vacuum. The vacuum is applied at the ground surface or through extraction wells. The method is applicable to the remediation of permeable soils contaminated by medium to high volatility organics. The technology suffers from the same disadvantages as air stripping, namely, limited applicability and relatively slow treatment (Ghassemi, 1986). Field studies are described in Applegate, 1987.

RADIO FREQUENCY HEATING

Electromagnetic (EM) energy is applied to the soil either at the ground surface or through boreholes (Dev, 1986). The EM energy heats the soil and decontaminates the soil in one of two ways, thermally or chemically. In the first case, the contaminants are vaporized and recovered at the surface and, in the latter case, the heat is used to assist in the reaction between the contaminant and a chemical agent injected into the soil. The method is best suited to contaminants such as chlorinated hydrocarbons, PCBs, benzene and toluene. There have been no full field scale evaluation of this technique as far as the authors are aware.

SUPERCRITICAL SOLVENT EXTRACTION

In this method, the contaminant is extracted with a material in its supercritical state, achieved by a certain combination of temperature and pressure (e.g., carbon dioxide at high pressure and moderate temperature). In this state, the extraction agent has a high relative density and a large capacity to dissolve the contaminant but still has relatively good fluidity. Following extraction the waste compounds can be completely precipitated from the solvent by means of a drop in pressure to below the solvent's critical conditions. The method has only been used on small laboratory samples to date (Groves, et al., 1985).

There are also soil stabilization techniques whereby the contaminant is not "flushed" out of the soil but treated "in-place". They are grouped as physical, chemical and biological.

PHYSICAL STABILIZATION

One example (there are certainly others) of this technique is being pursued by Battelle Pacific Northwest Laboratories (Fitzpatrick, et al., 1986). In this treatment, electrodes are placed in the ground and the soil is electrically heated to about 3600°F, which pyrolyzes the organics and drives off the gases (to be collected at the surface). The inorganics are trapped within the vitrified glass (made from the soil) and thereby rendered immobile. Additionally, a great many other physical stabilization agents have been tried, e.g., concrete, polymers, etc.

CHEMICAL STABILIZATION

Chemical stabilization of contaminated soils is commonly brought about by mixing the soil with additives to form a stable mass in which the contaminants are entrapped or micro-encapsulated. The process alters the chemical form of the contaminant to make it less soluble and/or less reactive (Betteker, et al., 1986). Two of the most common additives used are Portland cement and lime. Often accompanying the stabilization is an improvement of soil properties, such as an increase in bearing capacity and a decrease in permeability. Adequate mixing of the soil and additive is essential to insure contact between the contaminant and additive.

BIOLOGICAL STABILIZATION

Although biological treatment is geared toward groundwater remediation, it does show some promise for the contaminated vadose zone. Hydrocarbons can be degraded in soil by bacteria (possibly purposely injected) and other microbes to form more microbes, carbon dioxide and water. In order for biodegradation to occur, the microbes must be exposed to oxygen, moisture and nutrients, such as nitrogen and phosphorus. The rate of biodegradation is highest near the surface of the soil and decreases with depth due to decreasing amounts of oxygen and nutrients (Davis, 1972). One possible situation for the use of biodegradation is the addition, by injection wells, of nutrients and possibly an active bacterial seed into the contaminated soil to enhance the growth of existing bacteria. Unfortunately, the products of biodegradation may be toxic or harmful in some other way. Much research work needs to be done with this method.

The steam stripping technique is discussed last here because it is the subject of the present paper.

STEAM STRIPPING

In this technique, steam is injected into the contaminated soil. When the vapor pressure of the steam plus the vapor pressure of the contaminant equals the ambient pressure, the "mixture" of steam plus contaminant will "boil-off". Steam stripping is used commercially to regenerate solids, e.g., chemical processing tank bottoms, and as an analytic technique to analyze materials, e.g., the Nielsen-Kryger steam distillation procedure to analyze residual chemical contents of soil (Dev, 1986). There have been two reports of its use to clean contaminated soil (Toxic Treatment, Inc, 1986, Hilberts, 1985).

Much work remains to be done in understanding the actual processes involved in steam stripping a chemical from different types of soils.

BACKGROUND OF PROJECT AND PREVIOUS WORK

The overall goal of the project is to design a field-deployable vacuum-assisted steam stripping unit that will remove pollutants from contaminated soil and collect them above ground. To this end, a detailed literature search has been performed and small scale laboratory studies have been run. The laboratory studies have involved:

- Experiments in a relatively large, thin transparent box to observe two-dimensional flow of steam in a variety of soils. This allowed a determination of transient flow times, gave a general idea of relative steam permeabilities in various soils and allowed visual observations of steam flow.

- Small scale experiments on steam stripping of gasoline from two types of soils. This work gave support to the idea that steam stripping is a viable method to decontaminate a wide variety of soils.

- Preliminary successful operation of a small scale geosynthetic containment system. A unique feature of the present steam stripping unit is a cap assembly made of geosynthetic components. This cap will contain and collect the steam and pollutants stripped from the soil.

The results of our work to date can be found in Lord, et al. 1987a and Lord, et al. 1987b. The present paper develops an analytical, full-scale field model and describes the experiments that provide the data needed to use the model for predicting treatment times, removal efficiencies, etc., during steam stripping field decontamination.

ANALYTICAL MODEL FOR FIELD STEAM STRIPPING

The model for field steam stripping is shown in Figure 1. It is assumed that the soil is homogeneous, isotropic and described by a steam permeability coefficient, k. A steam pipe of radius r_p and carrying a steam pressure P_p (above atmospheric pressure) is imbedded at a depth of d below the ground surface. The solid lines in Figure 1 are the flow lines and the dashed lined are the equi-potential lines. Note that the ground surface is an equi-potential surface (namely, atmospheric or a constant negative pressure when a vacuum is applied to the surface). It is assumed that there are no sources or sinks for steam flow and it flows as a simple ideal gas*. In the steady state the steam pressure, P, satisfies Laplace's equation,

$$\nabla^2 P = 0. \tag{1}$$

It is convenient to work in spherical coordinates, with only radial coordinate, r, dependence; therefore,

$$\nabla^2 P = \frac{1}{r^2}\left[\frac{d}{dr}\left(r^2 \frac{dP}{dr}\right)\right] = 0. \tag{2}$$

Thus

$$\frac{d}{dr}\left(r^2 \frac{dP}{dr}\right) = 0. \tag{2a}$$

Integrating twice, we obtain

---

*Heat flow effects are not included in this simple analysis.

$$P = \frac{C_1}{r} + C_2 , \tag{3}$$

where C_1 and C_2 are constants and r is the radial dimension. The model shown in Figure 1 is solved by the method of images with an equal size sink located at a distance d above the ground surface (see Figure 2). The pressure at point r in the soil is given from Equation 3 as

$$P(r) = \frac{C_1}{r_1} - \frac{C_1}{r_2} + C_2 , \tag{4}$$

where C_1 and C_2 are to be determined from boundary conditions and r_1 and r_2 are shown on Figure 2. At the pipe surface,

$$P = P_p$$

$$r_1 = r_p$$

$$r_2 = 2d$$

and, at the ground surface (y=0), we set the steam pressure equal to zero. Thus,

$$P(y = 0) = 0 = \frac{C_1}{r_1(y=0)} - \frac{C_1}{r_2(y=0)} + C_2 , \tag{5}$$

and, with r_1 (y=0) = r_2 (y=0), $C_2 = 0$.

Also,

$$P(\text{pipe}) = P_p = C_1\left[\frac{1}{r_p} - \frac{1}{2d}\right] \qquad \text{or} \tag{6}$$

$$C_1 = \frac{P_p}{\left[\frac{1}{r_p} - \frac{1}{2d}\right]} , \tag{6a}$$

$$P(r) = \frac{P_p}{\left[\frac{1}{r_p} - \frac{1}{2d}\right]}\left[\frac{1}{r_1} - \frac{1}{r_2}\right] . \tag{7}$$

In terms of the rectangular coordinates (shown in Figure 2, where z is perpendicular in to the paper),

$$P(r) = \frac{P_p}{\left(\frac{1}{r_p} - \frac{1}{2d}\right)} \left\{ \frac{1}{\left(x^2 + (y-d)^2 + z^2\right)^{1/2}} - \frac{1}{\left(x^2 + (y+d)^2 + z^2\right)^{1/2}} \right\} . \qquad (8)$$

Using an effective Darcy's law, we can obtain the velocity components of the steam flow

$$\vec{v} = -k\vec{\nabla}P \ , \qquad (9)$$

where

v is the steam velocity
k is the permeability of the steam in the soil, and
$\vec{\nabla}P$ is the steam pressure gradient.

The y-component of velocity is given by

$$\begin{aligned} v_y &= -k \frac{\partial P}{\partial y} \\ &= \frac{-k\ P_p}{\left[\frac{1}{r_p} - \frac{1}{2d}\right]} \left\{ \frac{-(y-d)}{\left(x^2+(y-d)^2+z^2\right)^{3/2}} + \frac{(y+d)}{\left(x^2+(y+d)^2+z^2\right)^{3/2}} \right\} . \qquad (10) \end{aligned}$$

At the ground surface, i.e., y = 0 on Figure 2, Equation (10) reduces to

$$v_y(y=0) = \frac{-k\ P_p}{\left(\frac{1}{r_p} - \frac{1}{2d}\right)} \frac{2d}{\left(r^2 + d^2\right)^{3/2}} \ , \qquad (11)$$

where

$$r = \sqrt{x^2 + z^2} \ .$$

The incremental steam outflow through an annular region from r to r + dr is (see Figure 3)

$$dQ = \left[v_y(y=0)\right] 2\pi r \, dr. \tag{12}$$

If the collecting area on the surface extends from 0 to R, then the total amount of steam collected is

$$\int_0^R dQ = - \frac{4\pi \, kP_p d}{\left(\frac{1}{r_p} - \frac{1}{2d}\right)} \int_0^R \frac{r \, dr}{\left(r^2 + d^2\right)^{3/2}} \; . \tag{13}$$

This gives

$$Q(R) = \frac{-4\pi \, kP_p d}{\left[\frac{1}{r_p} - \frac{1}{2d}\right]} \left[\frac{1}{d} - \frac{1}{\left(R^2 + d^2\right)^{1/2}}\right] . \tag{13a}$$

The minus sign enters due to the fact that the y-direction is taken as positive downward. If the collection is over the entire ground surface, i.e., $R \to \infty$,

$$Q = \frac{-4\pi \, k \, P_p}{\left[\frac{1}{r_p} - \frac{1}{2d}\right]} \; . \tag{14}$$

Equation (13a) can be written in the following form

$$Q(R) = \frac{-4\pi \, k \, P_p}{\left(\frac{1}{r_p} - \frac{1}{2d}\right)} \left[1 - \frac{1}{\left(1 + \frac{R^2}{d^2}\right)^{1/2}}\right] . \tag{13b}$$

A very useful quantity is the flow rate/area through an annular region. This is derived as

$$\frac{dQ}{dA} = \frac{dQ}{dR} \frac{dR}{dA} , \tag{15}$$

where

$$A = \pi R^2 \; . \tag{16}$$

Using Equations (13b), (15) and (16), this becomes

$$\frac{dQ}{dA} = \frac{-2\ kP_p}{\left(\frac{1}{r_p} - \frac{1}{2d}\right)} \cdot \frac{1}{\left(1 + \frac{R^2}{d^2}\right)^{3/2}} \quad . \tag{17}$$

This quantity is shown as a function of R/d in the lower curve of Figure 4. If many steam tubes are placed in a regular square array (all at same depth d) the flow rate becomes more uniform. The upper curve in Figure 4 corresponds to the surface flow rate when the tubes are spaced uniformly in a 2-D array, with a lateral spacing equal to the depth d. The calculation is approximate because it sums only the contributions from nearest tubes and next nearest tubes. The middle curve corresponds to a uniform array with spacing equal to 2d. Again, it must be emphasized that the curves only correspond to an approximate flow rate. The upper two curves of Figure 4 are presented only to indicate the strong trend toward lateral surface steam flow uniformity when arrays are used (versus the strong lateral nonuniformity when a single tube is used - the lower curve of Figure 4).

To apply the model developed the following information must be supplied:

- values of r_p, d and P_p
- time it takes the steady state to be achieved, i.e., essentially how long it takes the steam front to reach the surface
- k-values for a given soil type
- stripping efficiency for a given soil/chemical combination
- total surface flow rate as a function of pipe depth and pipe spacing. This point requires further numerical work but, for the present paper, it will be assumed that the result of Equation (14) applies for each tube and that the total flow rate is the number of tubes times the flow rate of each tube. (This neglects the beneficial effect (for chemical stripping) of increased soil temperature when many steam tubes are used).

EXPERIMENTAL DETAILS

The following experiments were performed to obtain data for use in the analytical model.

STEAM FRONT MOVEMENT (2-D)

The steam front movement was observed in a Plexiglass cell 3 ft x 2 ft x 1 in thick. Steam from the house line, at about approximately 6 lb/in^2 and slightly above 100°C, was injected into the center of the soil-filled cell and dimensional measurements were made of the expanding steam front versus time. A variety of soil types were used in the present study. These are characterized in Table I. The cell was instrumented with temperature sensors on a 6-in. square array. (Details of the cell and results can be found in Lord, et al., 1987b). The results obtained with the cell gave visual information in regard to general behavior of steam fronts in a variety of soil types and in particular transient flow times.

STEAM PERMEABILITY IN SOILS

One dimensional standard-type permeability measurements were made with Plexiglass cylinders of 2.5-in. diameter and 6-in. high. They were filled with the various soils (properties listed in Table I) and house steam was passed through them, condensed in a specially built copper coil condenser immersed in cooled ethylene glycol maintained at about 5°C and collected in a flask. In most cases, vacuum (up to 20 in. Hg) was applied to the outlet side of the condenser to facilitate steam flow (and steam stripping in the case of chemically-spiked soil). Figure 5 shows a schematic diagram of the experimental setup. The permeability was determined by standard means using the pressure difference, area and lengths of the soil column and the flow rate.

STEAM STRIPPING OF CHEMICALS FROM SOIL

The same setup shown in Figure 5 was used to determine the steam stripping removal efficiency of various chemicals from the soils. In this case, the chemical was placed uniformly in the originally-dry soil at a given degree of saturation, and then steam was introduced into the cell. The amount of steam plus chemical that condensed was measured as a function of time. The condensed mixture was shaken vigorously and allowed to settle for a few hours. The chemicals used had a very limited solubility in water, so reasonably complete separation took place in the liquid state. Thus the amount of condensed steam and chemical were read by simple volumetric means.

RESULTS

STEAM FRONT MOVEMENT (2-D)

Figure 6 shows the results of the average radius (r) of the steam front versus time (t) for sand. The data is plotted on a log-log scale in Figure 7 to see if there is a power law of the form

$$r = Ct^n \, . \tag{18}$$

(A value of n = 1/2 would indicate simple diffusion.*) The relation seems well behaved out to a time of 36 minutes and the n-value is 0.54, very close to n = 1/2. The results of the power law fit of the data for the various soils are shown in Table II. (The value of C is difficult to determine, because the time for the steam front to appear is not well defined experimentally.)

If it is assumed that the outward flows observed are purely diffusive steam flows that obey Fick's second law, then we can use Equation 18 with n = 1/2 to predict transient flow times. For example using the data of Table II it is possible to determine in an approximate manner how long it would take the steam front to reach the surface in any soil type. Let's use a pipe depth of 5 feet in sand

$$\frac{t_{5\text{-ft}}}{t_{1\text{-ft}}} = \frac{(5)^2}{(1)^2} ,$$

$$\begin{aligned} t_{5\text{-ft}} &= 25\ t_{1\text{-ft}} \\ t_{5\text{-ft}} &= (25)(25\text{ min}),\ \text{where } t_{1\text{-ft}} = 25\text{ min}, \\ &= 625\text{ minutes} = 10.4\text{ hrs.} \end{aligned}$$

Thus, in sand, it would take 10.4 hrs for the steam to reach the surface after start of flow from a pipe opening at a depth of 5 ft. The above estimate is conservative for it is based on a two-dimensional diffusion process and the actual problem in the field is three dimensional. On a relative basis, diffusion takes place faster, the larger the dimension (Holman, 1972; Schneider, 1955). A rough rule would be that the constant in Eqn. (18) varies as the square root of the dimension. That is, the field times predicted from the two-dimensional experiments will be too long by a factor of

$$\frac{\sqrt{3}}{\sqrt{2}} = 1.22.$$

STEAM PERMEABILITY OF SOILS

Figure 8 shows the volume of water (condensed steam) passing through the permeability cell as a function of time for the various soils. From this type data the permeability, k, is determined from

$$k = \frac{Q_{1D}}{\left(\frac{\Delta P}{\Delta l}\right) A} \qquad (19)$$

where

---

*A constant rate of steam input would also produce a $t^{1/2}$ dependence in this two dimensional experiment.

Q_{1D} is the flow rate in the one-dimensional flow
ΔP is the total (positive and negative) pressure differential across the cell
Δl is length of the cell, and
A is the area of the cell.

To determine k-values in conventional units of (cm/sec), the ΔP value is converted to an equivalent hydrostatic head. Table III gives the steam permeability values for the various soils used in the study. The values for water permeability, determined with a standard constant head permeameter are also given in Table III for comparison.

STEAM STRIPPING OF CHEMICALS FROM SOIL

The work in this paper will be involved with grade A-kerosene as the "chemical". (More chemicals will be used in subsequent work). For all tests reported here, the saturation was at 25% kerosene. (The soil was initially dry.) Figure 9 shows the results of steam stripping of kerosene from the various soil types. Figure 8 shows that the steam output rate for each soil was a constant. Figure 9 however shows that the rate of removal of kerosene is very strongly a function of the soil type and time. The reduced rate of removal for the higher silt content soils cannot be explained simply by the reduced permeabilities. The kinetics of removal is certainly a complicated process and must be researched further for the various soil types. The results of all the kerosene steam stripping runs are presented in Table IV. In this table are presented the following quantities for kerosene steam stripped from each soil

$S_{i.r}$ = the initial rapid removed percentage (that which takes place in the very first few minutes)
$t_{i.r}$ = the time for the initial rapid removal
S_{60} = the removed percentage at 60 minutes
S_{180} = the removed percentage at 180 minutes
$t_{c.r.}$ = the (extrapolated) time for complete removal
P = the number of pore volumes (extrapolated from the data) of condensed steam needed to decontaminate the sample

USE OF THE FIELD MODEL

Here we shall use the data obtained in the experimental portion of the project to derive pertinent field information from the analytical model developed earlier in the paper. A problem arises in the use of multiple steam pipes (which will almost always be the case in the field) for a complete sum of the contributions from all tubes in the array must be given, and not just the contributions from nearest and next nearest tubes (see Fig. 4). However these summations are not available at present. Therefore, it will be assumed that each tube gives a flow rate contribution equal to that given in Equation (14). This assumes that lateral barriers are placed on the periphery of the site and "channel" all the outward flowing steam to the surface. (The effect of temperature has not been considered in the model.)

The use of multiple steam tubes will increase the temperature somewhat, but the actual effect is unknown at present.)

Thus the following approximation will be used for the total flow to the surface from n imbedded steam pipes

$$Q_{TOTAL} = n \frac{4\pi\,(k\Delta P)}{\left[\dfrac{1}{r_p} - \dfrac{1}{2d}\right]}\,, \tag{14a}$$

where $\Delta P = P_p$.

(We have dropped the minus sign for convenience.) The product $k\Delta P$ can be obtained most readily from the one-dimensional permeability studies (assuming the same k applies for both laboratory and field).

The field model will be used with the following example (see Figure 10). A kerosene spill in sand of pore volume = 40% covers a circular area with a 5 meter (~15 ft) radius. The spill has penetrated uniformly to a depth of 0.6 meters (~2 ft). The saturation of the kerosene in the originally dry soil is uniform and has a value of 25%. Five steam pipes (in a regular array) are inserted to a depth of 1.7 meters (~5 ft). The pipes each have an inner radius of 0.05 meters (~2 in.). Using the data of Figure 8 for the sand, the value of $k\Delta P$ is found (for 6 psi steam pressure) to be

$$k\Delta P = \frac{Q_{1D}\Delta l}{A} \tag{19a}$$

$$= 1.76 \times 10^{-5}\ \frac{m^2}{s}\ (\text{for } \Delta P = 6 \text{ psi})$$

(SI units will be used subsequently in these model evaluations for future consistency.) The product $k\Delta P$ will be used in the subsequent calculations, without separating out the k-term explicitly.

Putting these parameters in Eqn. (14a) we obtain

$$Q_{TOTAL} = 5\,\frac{4\pi\left(1.76 \times 10^{-5}\right)}{\left[\dfrac{1}{0.05} - \dfrac{1}{2(1.7)}\right]} =$$

$$= 5.6 \times 10^{-5}\ \frac{m^3}{s}$$

Using the extrapolation to 100% removal from Figure 9 and the flow rate from Figure 8, it is seen that 22,400 ml of condensed steam must flow through the cell to complete* the removal of kerosene for the sand sample. The measured porosity of the sand sample was 39%. Thus with a sample volume of 456 cm^3 there is 178 cm^3 of pore space. Therefore, if laboratory and field situations are equivalent, it requires 22,400/178 = 126 pore space volumes of steam to pass through to totally decontaminate the soil. Referring to the model field situation of Figure 10, we see that there is a pore space in the contaminated region of

$$\pi(5)^2(0.6)(0.40) = 18.84 \text{ m}^3$$

Thus if 126 pore space volumes of steam are needed, a total flow of steam of

$$18.84 \times 126 = 2374 \text{ m}^3$$

is required to decontaminate the soil. With the Q_{TOTAL} calculated previously, it is seen that it will take a time of

$$t = \frac{2374}{5.6 \times 10^{-5}} = 4.23 \times 10^7 \text{ sec} = 16.3 \text{ months}$$

to decontaminate our "model spill" with the steam stripping technique. It must be emphasized that this result applies only for a steam pressure of 6 psi and a pipe radius of 0.05 meters. Results for decontamination times using other (possibly more realistic) combinations of steam pressures and pipe radii are given in Table V. In formulating Table IV, it is assumed that the permeability is independent of pressure.

In Table V we tabulate the:

- time for steam flow to reach the surface
- pore volumes of steam needed to decontaminate the model spill
- steam flow rate at various combinations of ΔP and r_p
- time needed to decontaminate the model spill at various combinations of ΔP and r_p.

A typical field situation might be $\Delta P = 50$ psi and $r_p = 0.05$ m. According to Table V, this would involve decontamination times of 1.95 months in a sand, 4.45 months in a 75% sand/25% silt soil and 8.2 months for the 50% sand/50% silt. (The 25% sand/75% silt data does not seem to go out far enough in time for a reliable extrapolation, and possible "steam fracturing" precludes using the method in 100% silt. These times do not appear to be prohibitively long. The results for other combinations of pressure and pipe radius can be obtained from Table V.

---

*Our analytical technique is estimated to be good to ±2%, so in the ultimate sense the kerosene may not be completely removed.

CONCLUSIONS

The project is involved with steam stripping of contaminants from polluted soil. Steam pipes are driven into the ground in an array, and are used to deliver steam to the subsurface. The steam moves through the soil and "strips" the contaminant from the soil voids and that attached to the soil particles and carries them to the surface where they are collected. The collection system is a unique geosynthetic cap assembly, which is connected to a vacuum system to enhance collection (the geosynthetic cap is described in Lord 1987b).

In the portion of the work reported here, an analytical model is developed for the field steam stripping. The data necessary to use the model for predictive purposes are generated in a series of experiments in a variety of soils which include:

- observations of the transient steam front movment in two-dimensions
- measurements of steam permeability in one dimensional experiments
- measurements of steam stripping efficiency of kerosene in one-dimensional experiments.

The data so obtained was used in the analytical model to predict such things (in a variety of soils, at different steam pressures and pipe sites) as the:

- time for steam front to reach ground surface
- total surface steam flow rate from a series of embedded pipes
- time needed to decontaminate a given spill of kerosene.

From the work reported here, it appears that with future developmental work steam stripping can become a viable technique with which to clean up spills.

Future work is projected to include:

- steam stripping efficiency of kerosene in the 25% sand/75% silt soil for longer periods of time than reported here
- steam stripping efficiency for a variety of simple chemicals from the various soils
- steam stripping efficiency versus vacuum extraction and hot air extraction
- large scale laboratory experimental test of the analytical model
- collection efficiency of the geosynthetic cap
- steam stripping at higher steam pressures
  In the field, higher steam pressures will certainly be used. The analytical model developed here shows that the decontamination time will vary as the inverse of the steam pressure. However an upper limiting pressure will be reached where the high pressure will

"fracture" the soil and produce cracks which could extend to the surface and produce preferential steam paths (thus precluding uniform steam treatment of the soil). Work to date (Lord, et al., 1987b) has shown that this fracturing takes place at steam pressures of 6 psi with a pure silt soil ($k = 3 \times 10^{-6}$ cm/sec). For more permeable soils, higher pressure will probably produce fracturing.

- Evaluation of the method at actual field sites.

ACKNOWLEDGMENTS

The Drexel authors wish to thank the Hazardous Waste Research Engineering Laboratory of the U. S. EPA of Edison, New Jersey for their financial support of this work through Cooperative Agreement No. CR-813022-01.

REFERENCES

Anastos, G., Corbin,M. H., and Coia, M. F. (1987). "In Situ Air Stripping of Soils: Field Pilot Studies Through Implementation." _Proceedings, 19th Mid-Atlantic Industrial Waste Conference_, Bucknell University, Edited by Jeffery C. Evans, Technomic Pub. Co., Inc, Lancaster, PA, pp. 163-171.

Applegate, J., Gentry, J. K. and Malot, J. J. (1987). "Vacuum Extraction of Hydrocarbons From Subsurface Soils at a Gasoline Contamination Site," _Proceedings, Superfund '87_, pp. 273-279, Washington, DC, November, 1987, published by Haz. Mat. Control Res. Inst., Silver Spring, MD.

Betteker, J. M., Sherrad, J. H. and Ludwig, D. L. (1986). "Solidification/Stabilization of Contaminated Dredged Material," _Proceedings, 18th Mid-Atlantic Industrial Waste Conference_, Virginia Polytechnic Institute and State University, Edited by Gregory D. Boardman, Technomic Pub. Co., Inc., Lancaster, PA, pp. 253-273.

Cheremisinoff, P. N. (1987). "Update: Hazardous Waste Treatment," *Pollut. Engin.* 19, pp. 42-49.

Davis, J. B., Farmer, V. E., Kreider, R. E., Straub, A. E. and Keese, K. M. (1972). The Migration of Petroleum Products in Soil and Groundwater: Principles and Countermeasures," *American Petroleum Institute,* Washington, DC, Publication E4149, December, 1972.

Dev, H. (1986). "Radio Frequency Enhanced In-Situ Decontamination of Soils Contaminated with Halogenated Hydrocarbons," _Proc. of EPA Conf. on Land Disposal, Remedial Action, Incineration and Treatment of Hazardous Waste_, Cincinnti, Ohio, April 1986, published by EPA Haz. Waste Engin. Res. Lab., Cincinnati, Ohio.

Fitzpatrick, V. F., Timmerman, C. L. and Buelt, J. L. (1986). "In-Situ Vitrification - A Candidate Process for In-Situ Destruction of Hazardous Waste," _Proceedings, Seventh Superfund Conference_, Washington, DC, November

1986, published by HMCRI.

Ghassemi, M. (1986). "Innovative In Situ Treatment Technologies for Cleanup of Contaminated Sites," *Proceedings, Third Annual Hazardous Waste Law and Management Conference*, sponsored by U. S. EPA and Northwestern School of Law, Oct. 29 and 30, 1986, Seattle, Washington.

Groves, F. R., Brady, B. and Knopf, F. C. (1985). "State-of-the- Art on the Supercritical Extraction of Organics from Hazardous Wastes," CRC Critical Reviews in Environmental Control, Vol. 15, No. 3, pp. 237-274.

Hilberts, B. (1985). "In-Situ Steam Stripping," Assink, J. W., Van Den Brink, W. J., Eds., *Contaminated Soil*, Proc. of 1st Intern. TNO Conf. on Contaminated Soil, Utrecht, The Netherlands, Nov. 11-15, 1985, pp. 680-687.

Hill, R. D. (1987). "Superfund Innovative Technology Evaluation (SITE) after the First Year," *Proc. of Superfund '87 Conf. (8th National)* Nov. 16-18, 1987, Washington, DC, pp. 25-27, (HMRCRI).

Holmes, J. P.(1972). *Heat Transfer*, McGraw Hill, New York, Third Edition, Ch. 4.

Kovalic, J. M. and Kluccisk, J. F. (1987). "Loathing for Landfills Set Stage for Innovative Hazardous Waste Treatment Technology," Hazard Mat. and Waste Manage. *5*, pp. 17-18.

Lord, A. E., Jr., Koerner, R. M., Murphy, V. P. and Brugger, J. E. (1987a)."Vacuum-Assisted, In-Situ Steam Stripping To Remove Pollutants from Contaminated Soil," *Proc. of EPA Conf. on Land Disposal, Remedial Action, Incineration and Treatment of Hazardous Waste*, Cincinnati, Ohio, May 6-8, 1987, p. 511.

Lord, A. E., Jr., Koerner, R. M., Murphy, V. P. and Brugger, J. E. (1987b). "In-Situ, Vacuum-Assisted Steam Stripping of Contaminants from Soil," *Proc. of Superfund '87 Conf. (8th National Conf.)*, Nov. 16-18, 1987, Washington, DC, pp. 390-395, (HMRCI).

Schneider, P. J. (1955). *Conduction Heat Transfer*, Addison-Wesley Co., Cambridge, Mass., Ch. 10.

The Toxic Treatment Bulletin (1987). Vol. 1, No. 1, Published by Toxic Treatments (USA) Inc.

TABLE I. PROPERTIES OF THE SOILS USED IN THE PRESENT STUDY

Soil		Density	Porosity	Average Grain Size D_{50}	Grain Size Uniformity D_{60}/D_{10}
Sand (%)	Silt (%)	g/cm^3 (PCF)*	%	mm	
100	0	1.646 (102.7)	39	0.28	2.1
75	25	1.564 (97.5)	42.1	0.25	7.6
50	50	1.527 (95.3)	43.4	0.18	12.2
25	75	1.419 (88.5)	47.4	0.12	13.6
0	100	1.233 (76.7)	54.2	0.09	17.1

*PCF = pounds/ft^3

TABLE II. MOVEMENT OF STEAM FRONT IN TWO-DIMENSIONS

$r = Ct^n$

Soil		Value of n	Time for front to reach 12-inches (minutes)
Sand (%)	Silt (%)		
100	0	0.54	25
75	25	0.58	36
50	50	0.53	55
25	75	0.60	250
0	100	possible steam fracture	

TABLE III. STEAM AND WATER PERMEABILITIES

Soil		Standard Water Permeability	Steam Permeability	Steam Permeability / Water Permeability
Sand (%)	Silt (%)	(cm/sec)	(cm/sec)	-
100	0	1.38×10^{-3}	1.79×10^{-4}	0.13
75	25	2.06×10^{-4}	3.14×10^{-5}	0.15
50	50	8.82×10^{-5}	2.78×10^{-5}	0.31
25	75	9.61×10^{-5}	2.15×10^{-5}	0.22
0	100	3.6×10^{-6}	possible steam fracture	

TABLE IV. RESULTS OF LABORATORY SCALE 1-D STEAM STRIPPING EXPERIMENTS
(KEROSENE 25% SATURATION)

Soil		$S_{i.r.}$(%)	$t_{i.r}$ (min.)	S_{60} (%)	S_{180}(%)	$t_{c.r}$(min)	P
Sand (%)	Silt (%)						
100	0	60	~ 5	80	84	1120	126
75	25	45	~ 5	58	70	2600	147
50	50	20	~ 5	22	48	5300	239
25	75	10	~ 5	26	44	> than 50/50	> than 50/50
0	100	4	~ 5	7	17	> than 25/75	> than 25/75

$S_{i.r.}$ = the initial rapid removal
$t_{i.r}$ = time for initial rapid removal
S_{60} = amount removed at 60 minutes
S_{180} = amount removed at 180 minutes
$t_{c.r.}$ = extrapolated time for complete removal
P = the number of pore volumes (from extrapolation of data) of steam needed to decontaminate the sample.

TABLE V. EVALUATION OF STEAM STRIPPING FIELD MODEL
(THE MODEL SPILL IS SHOWN IN FIGURE 10.)

Soil		Time for front to reach surface (hrs)	Pore Volumes Needed to Decontaminate		Total Flow From Five Pipes (m^3/sec)	Time Needed to Decontaminate the Spill (mo.)
Sand (%)	Silt (%)		# of pore volumes	actual pore volume (m^3)		
100	0	10.4	126	2374		
r_p = 0.025 m						
p = 6 psi		"	"	"	2.8×10^{-5}	32.9
p = 25 psi					1.14×10^{-4}	7.9
p = 50 psi					2.28×10^{-4}	3.9
p = 100 psi					4.6×10^{-4}	2.0
r_p = 0.05 m						
p = 6 psi					5.6×10^{-5}	16.3
p = 25 psi		"	"	"	2.3×10^{-4}	3.9
p = 50 psi					4.6×10^{-4}	1.95
p = 100 psi					9.2×10^{-4}	0.98
r_p = 0.10 m						
p = 6 psi					1.14×10^{-4}	8
p = 25 psi		"	"	"	4.7×10^{-4}	1.9
p = 50 psi					9.3×10^{-4}	0.96
p = 100 psi					1.87×10^{-3}	0.48

TABLE V. - CONTINUED

Soil		Time for front to reach surface (hrs)	Pore Volumes Needed to Decontaminate		Total Flow From Five Pipes (m^3/sec)	Time Needed to Decontaminate the Spill (mo.)
Sand (%)	Silt (%)		# of pore volumes	actual pore volume (m^3)		
75	25	15	147	2769		
r_p = 0.025 m						
p = 6 psi					1.54×10^{-5}	69.5
p = 25 psi		"	"	"	6.5×10^{-5}	18
p = 50 psi					1.3×10^{-4}	9
p = 100 psi					2.6×10^{-4}	4.4
r_p = 0.05 m						
p = 6 psi					3.1×10^{-5}	34.5
p = 25 psi		"	"	"	1.3×10^{-4}	8.9
p = 50 psi					2.6×10^{-4}	4.45
p = 100 psi					5.2×10^{-4}	2.2
r_p = 0.10 m						
p = 6 psi					6.3×10^{-5}	17
p = 25 psi		"	"	"	2.6×10^{-4}	4.4
p = 50 psi					5.3×10^{-4}	2.2
p = 100 psi					1.06×10^{-3}	1.08

TABLE V. - CONTINUED

Soil		Time for front to reach surface (hrs)	Pore Volumes Needed to Decontaminate		Total Flow From Five Pipes (m^3/sec)	Time Needed to Decontaminate the Spill (mo.)
Sand (%)	Silt (%)		# of pore volumes	actual pore volume (m^3)		
50	50	22.9	239	4500		
$r_p = 0.025$ m						
$p = 6$ psi					1.25×10^{-5}	137
$p = 25$ psi					5.2×10^{-5}	32.9
$p = 50$ psi		"	"	"	1.04×10^{-4}	16.5
$p = 100$ psi					2.08×10^{-4}	8.3
$r_p = 0.05$ m						
$p = 6$ psi					2.53×10^{-5}	68
$p = 25$ psi					1.05×10^{-4}	16.3
$p = 50$ psi					2.1×10^{-4}	8.2
$p = 100$ psi					4.2×10^{-4}	4.1
$r_p = 0.10$ m						
$p = 6$ psi					5.14 x 1--5	33.5
$p = 25$ psi					2.13×10^{-4}	8.03
$p = 50$ psi					4.26×10^{-4}	4.04
$p = 100$ psi					8.53×10^{-4}	2.02

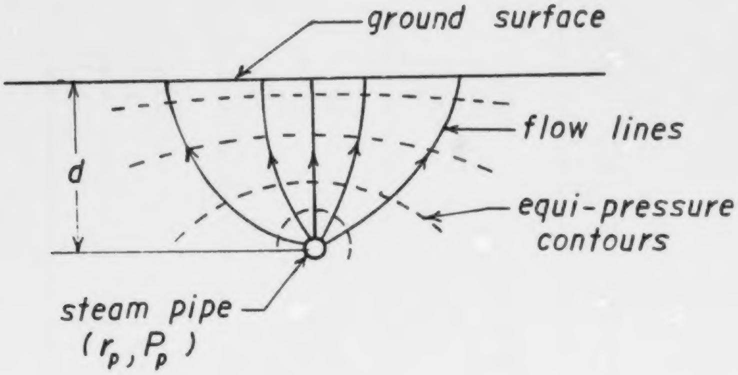

ground surface
flow lines
equi-pressure contours
d
steam pipe
(r_p, P_p)

Figure 1 - Model for steam stripping calculations.

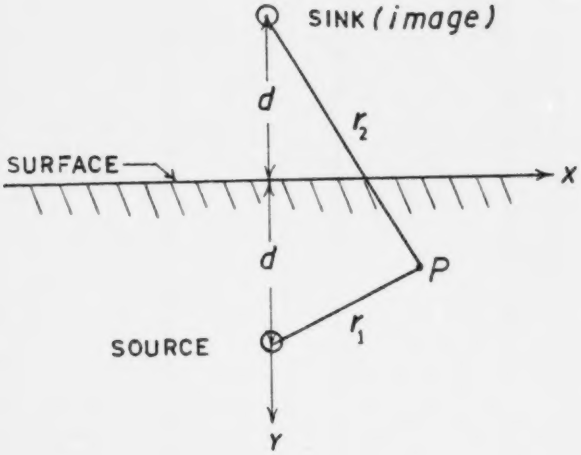
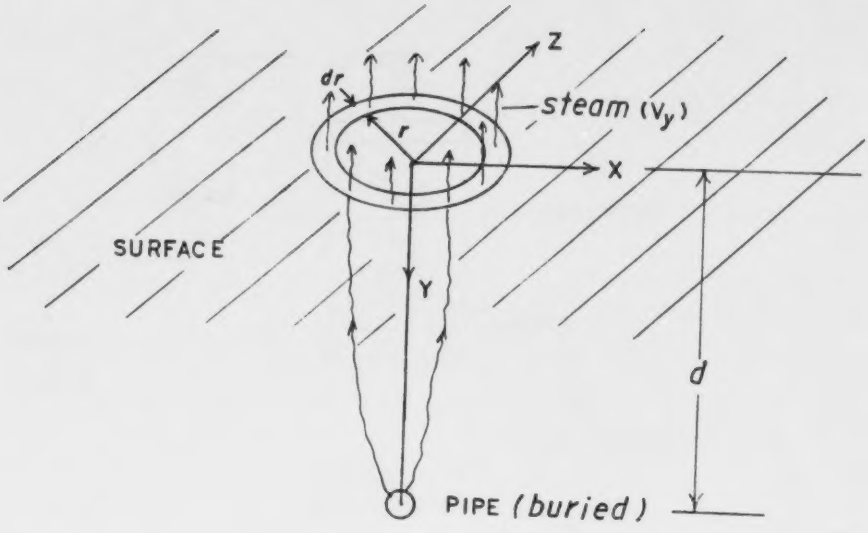

SINK (image)
d
r_2
SURFACE
x
d
P
r_1
SOURCE
Y

Figure 2 - Model of source and image to make surface an equipotential.



Z
dr
r
steam (v_y)
X
SURFACE
Y
d
PIPE (buried)

Figure 3 - Integrating the system outflow through the surface.

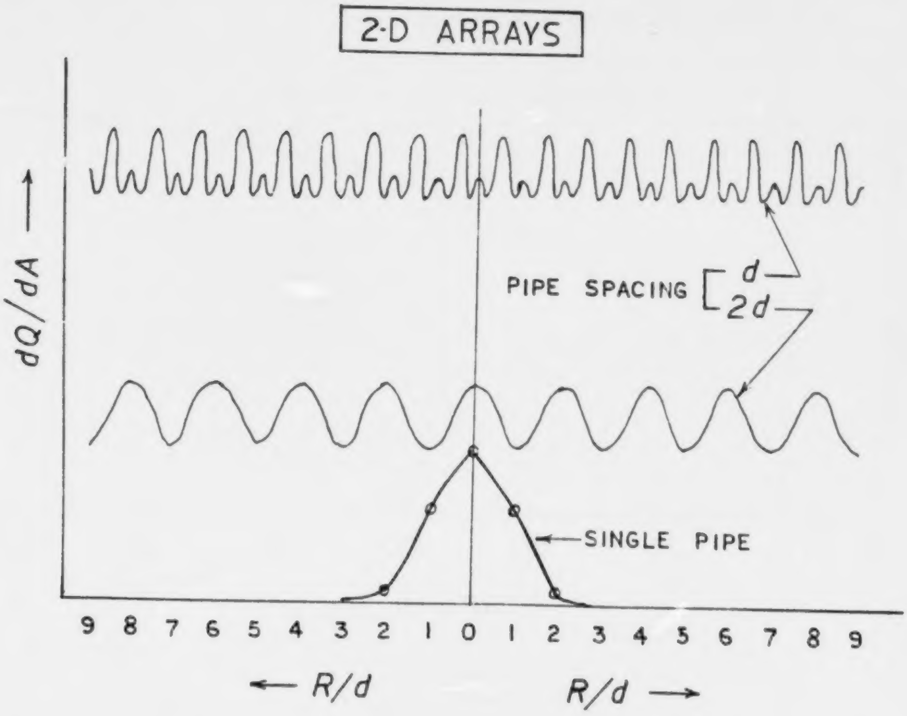


Figure 4 - Lateral dependence of steam outflow for various pipe arrays.

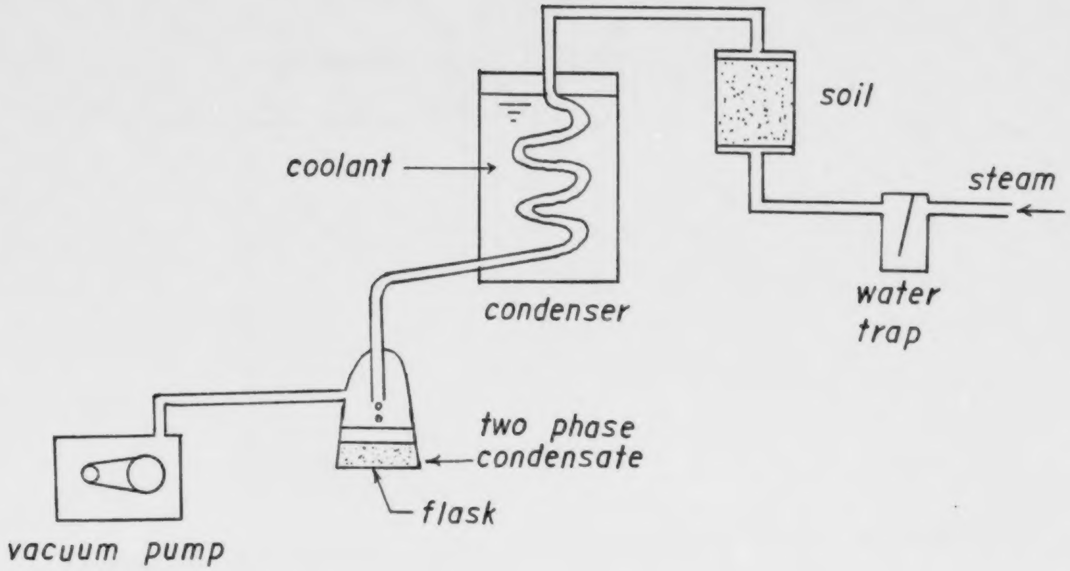

soil
coolant
steam
water trap
condenser
two phase condensate
flask
vacuum pump

Figure 5 - Schematic diagram of apparatus for determining steam permeability and steam stripping efficiency.

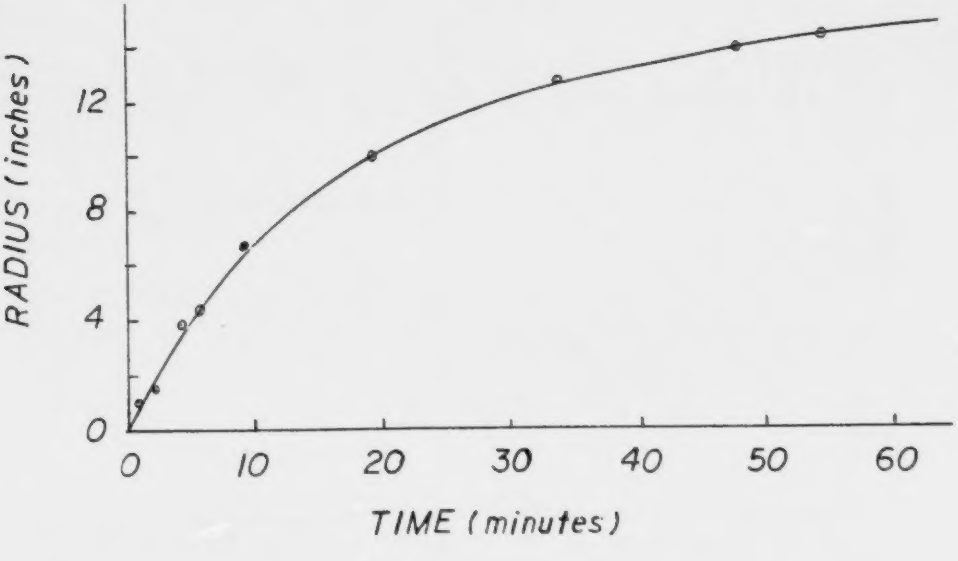


Figure 6 - Steam front radius versus time in the two dimensional flow box.

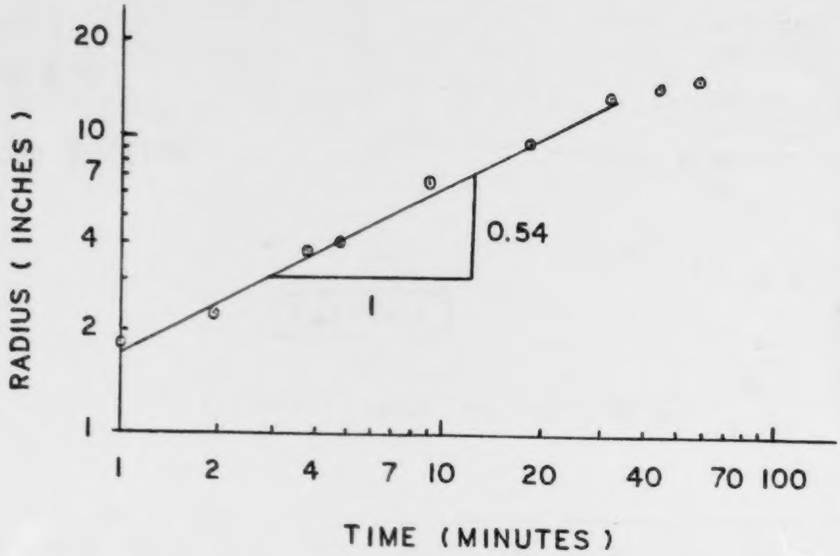


Figure 7 - Log-log plot of data of Figure 6 to determine power law.

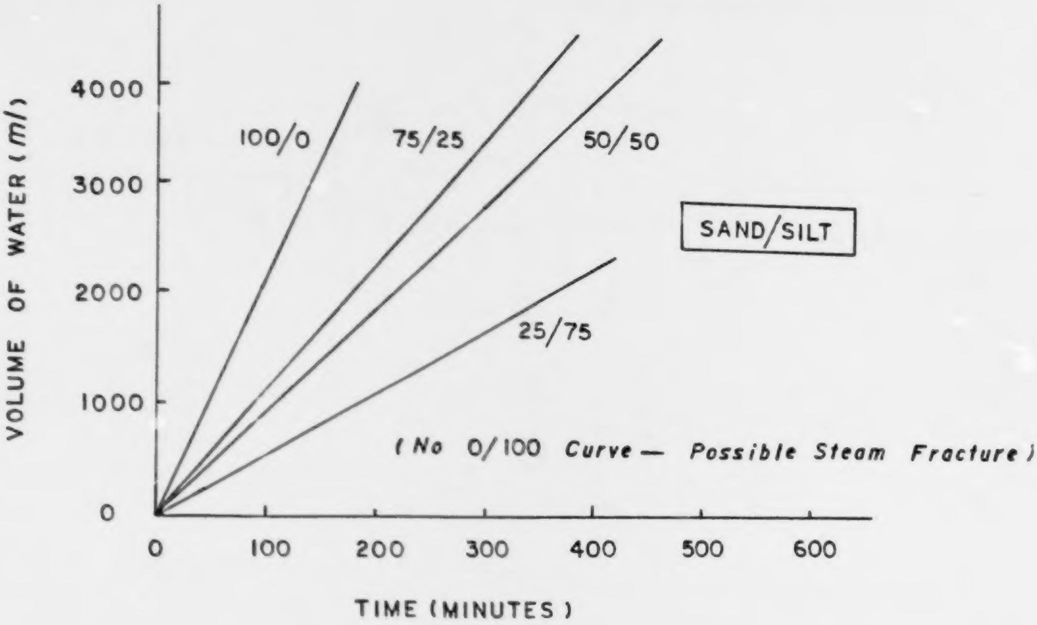


Figure 8 - One-dimensional flow rates of steam in the various soils. The data at 0/100 is affected by possible steam fracturing.

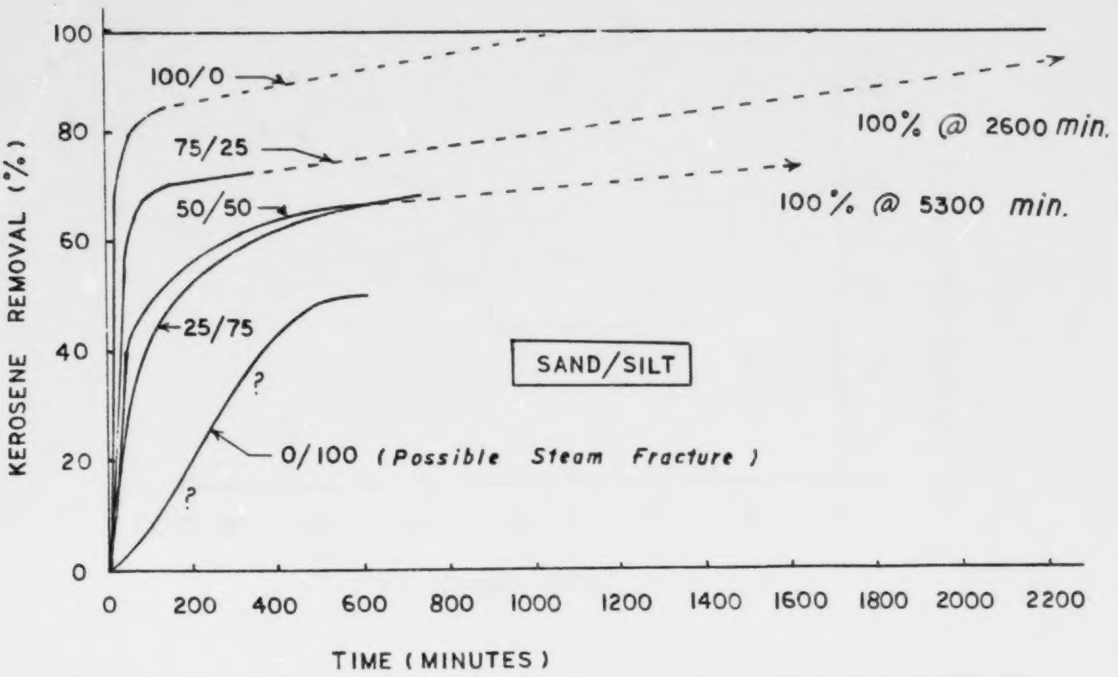


Figure 9 - Steam stripping efficiencies of kerosene from the various soils in the one-dimensional cells. The 0/100 is suspect because of possible steam fracturing.

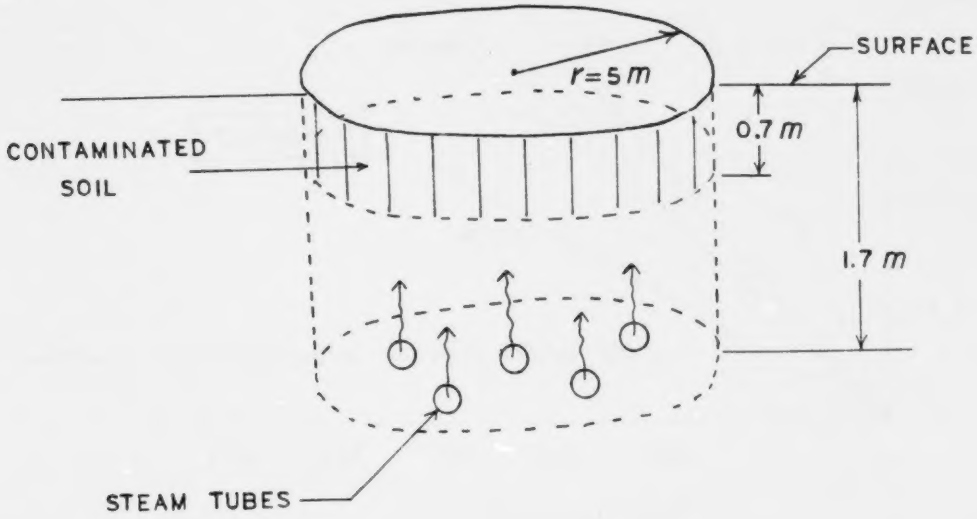

r=5 m
SURFACE
0.7 m
1.7 m
CONTAMINATED SOIL
STEAM TUBES

Figure 10 - Model field spill used in the analytical model for calculating steam stripping decontamination times.

USE OF FOAM TECHNOLOGY FOR CONTROL OF TOXIC GAS RELEASES

Patricia Brown
Enviresponse, Inc.
Edison, NJ 08837

Mark Torpey
Foster Wheeler Development Corp.
Perryville, NJ 08809

Gopal Gupta
Enviresponse, Inc.
Edison, NJ 08837

John Brugger
Releases Control Branch, USEPA
Edison, NJ 08837

ABSTRACT

In the wake of the Bhopal disaster, there is increasing public and governmental concern over the possibility of toxic gas and vapor releases from chemical plants. Industry is under intense pressure to provide additional safeguards to prevent "gas" clouds from threatening populated areas.

Many ways to prevent releases are already in use by industry, ranging from safety-conscious plant design, through safety alarms and interlocks, to backup devices such as scrubbers and flares. However, once a gas leak occurs, the options for its control are few.

Under study is the use of "foam scrubbing" as a new option for controlling emergency releases. Foam is to be generated from a concentrated fluid that contains neutralizing agents by use of the contaminated gas. Once the bubbles are formed, a large interior liquid surface area is available for gas, vapor, or particulate absorption. A neutralization agent present in the bubble walls then can react with the absorbed gas or vapor to render it innocuous.

This proposed technology has several potential applications to emergency control, among them, fixed installations in plants and portable units for emergency response teams. Foam technology may be applicable to various hazardous substances, including particulates and aerosols, gases and vapors.

INTRODUCTION

For many years, various types of foams have been used in fire-fighting applications. In these applications, foam is valuable for its ability to exclude air, wind, and sunlight and through self-drainage to slowly provide water to a fire. Developments in foam formulation have aimed at improvements in fire control, and enhanced extinguishing capabilities have led to improvement in vapor suppression characteristics.

Taking advantage of this latter benefit, recent work has focused on specific foam formulations to address the suppression of air pollutants. For the most part, these efforts have been primarily concerned with suppression of hazardous vapors or particulates from pools of spilled chemicals. Foam has the advantages of high surface area, positive control of vapors (through encapsulation), and capability for generation when and where needed. A neutralizing agent can be introduced with the liquid to render the absorbed gas or vapor innocuous. Foam generators potentially can be used as either fixed or portable installations, depending, for example, on whether they are used in a chemical plant to protect specific equipment or in the field by an emergency response team.

This paper addresses one application of foam, in which it is used to encapsulate contaminated air and scrub the contaminants therein. In particular foam scrubbing is investigated as a technique for alleviating the problem of "vapor cloud" releases. Judging from the literature, industry experience, and various calculations, the usefulness of foam in mitigating accidental chemical releases is indeed promising.

DESCRIPTION OF PROPOSED TECHNOLOGY

Figures 1, 2, and 3 illustrate several potential applications of foam scrubbing to the control of emergency releases.

- For an indoor plant with an existing ventilation system, a foam generator can be installed in the ventilation system near its exhaust point, as shown in Figure 1. Any accidental release of a gas (pressure relief, rupture disk, vessel failure) within the plant could be treated simply by turning on the foam generator or through automatic alarm/activation triggering by high contaminant concentration.

  Variations on this scheme include ductwork and a foam generator at grade (for heavier-than-air gases) or a foam generator mounted within the building. Use of a foam generator within the building would allow any untreated gas that might initially bypass the generator or otherwise escape the foam mass to be recycled until neutralized.

- Rapid, high pressure gas releases into the open atmosphere are the most difficult to detoxify. For an outdoor facility with potential leakage points such as flanges, loading connections, etc. that may permit formation of a vapor cloud, a foam generator can be used to collect the released

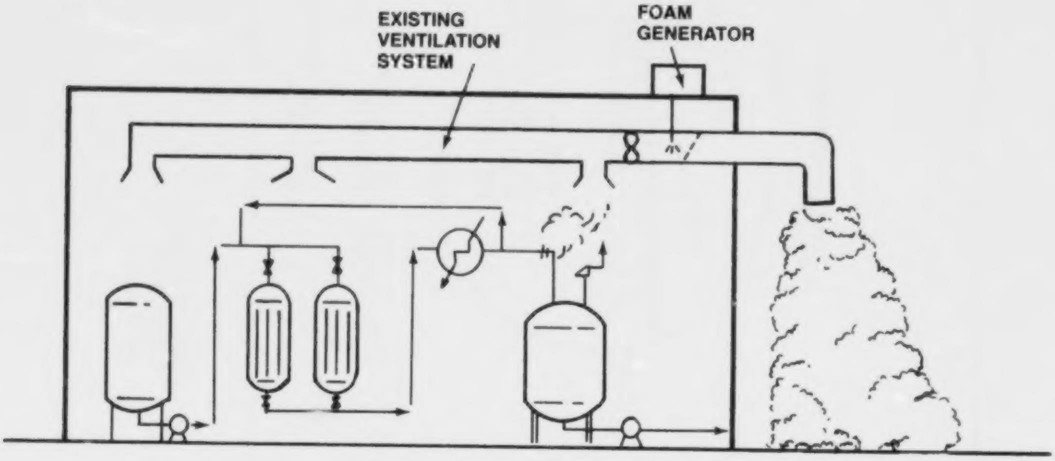
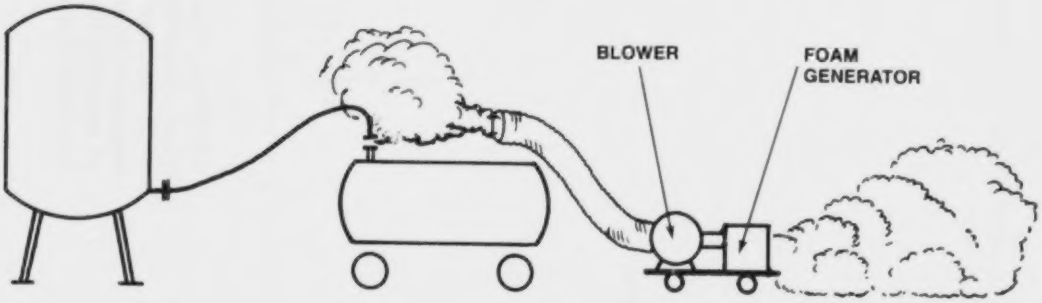
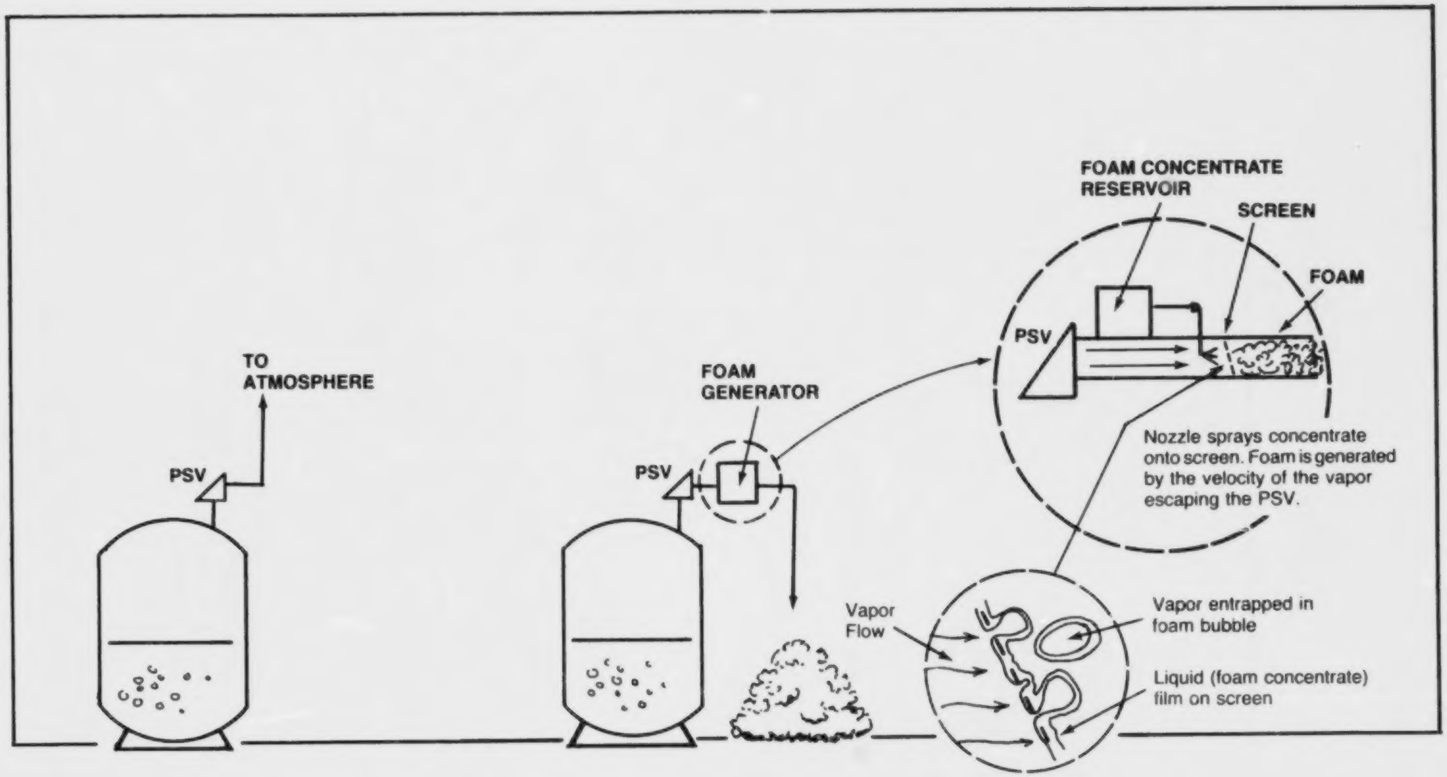

EXISTING VENTILATION SYSTEM
FOAM GENERATOR
ENCLOSED PROCESSING FACILITY

Figure 1. Schematic of an application of foam to mitigate vapor release at an indoor chemical processing facility.


BLOWER
FOAM GENERATOR

LOADING LINE BREAK OR MISALIGNMENT: Vapor release would be drawn under suction into foam generator.

Figure 2. Schematic of an application of foam to mitigate vapor release from miscellaneous sources.


FOAM CONCENTRATE RESERVOIR
SCREEN
FOAM
PSV
TO ATMOSPHERE
FOAM GENERATOR
PSV
PSV
Nozzle sprays concentrate onto screen. Foam is generated by the velocity of the vapor escaping the PSV.
Vapor Flow
Vapor entrapped in foam bubble
Liquid (foam concentrate) film on screen

TYPICAL EXISTING ARRANGEMENT: Vessel overpressure often results in vapor release to ambient environment.

POTENTIAL FOAM APPLICATION: Escaping vapor becomes entrapped in high-expansion foam, where it is neutralized. Foam piles up initially, ultimately collapses leaving "neutralized" liquid.

DETAIL OF FOAM GENERATION AT SCREEN

Figure 3. Schematic of an application of foam to mitigate vapor release from pressure safety valves (PSVs).

gases under suction, as shown in Figure 2. The generator can be either portable or centralized (depending on facility size), and the gases can be collected using a suction fan and flexible ducts. A portable version would be applicable for use by emergency response teams.

- There is the potential to place a foam generator at the discharge of a pressure safety valve (PSV), as shown in Figure 3, such that any escaping gas would generate foam using its own pressure. Calculations have shown that most gases at high concentration may not be directly treatable, since the heat required to neutralize high concentrations may destroy the foam. Therefore in such cases dilution air would need to be drawn into the foam in order to reduce the concentration of the toxic gas.

Based on the work of previous researchers (1-4) it is estimated that a foam with a collapse time on the order of one to two minutes would achieve adequate neutralization.

Handling of the foam once it has served its purpose--capture, neutralization, and collapse--could depend in part on the needs of the specific plant. In some instances, if the collapsed liquid is neutral and innocuous it could be allowed to drain naturally as is done with firefighting foam. Alternatively, the liquid could drain into a catch basin for collection, treatment, and environmentally acceptable disposal or potential reuse.

Use of foam for emergency control appears attractive because, unlike conventional equipment such as a scrubber, foam need not involve a large fixed installation. The foam generator and liquid reservoir are relatively small and can remain on standby until needed. At that time, foam generation can be triggered either by emergency personnel or by an automatic system. The foam mass itself can provide the residence time needed for control. This is in contrast to conventional equipment, in which residence time only can be increased by increasing the size of the unit.

High-expansion foam generators are produced commercially in sizes up to 30,000 cfm. This size would adequately control most leaks of concern to public safety. If higher capacity is required, custom built units can be used, or the release can be controlled using multiple units.

BACKGROUND ON FOAM

Aqueous foam is used in a number of diverse industries, including mineral processing (e.g., froth flotation), wastewater treatment (dissolved air flotation), textiles (dyeing, etc.), and food products (numerous food products including whipped cream, meringue, etc.) (5-7). One of the major uses of foam is in fire fighting, where it is of value for its capabilities to

- exclude air from a fire;
- supply water in controlled amounts; and
- suppress evaporation from pools of flammable liquid.

It is from the fire-fighting sector that applications to hazardous material control have arisen.

EPA has published a list of 406 Extremely Hazardous Substances (EHS) that are of particular concern if an emergency release should occur. (8) This list was reviewed to determine which of the chemicals are potential candidates for absorption into foam. The analysis was based on the expectation that any soluble gas, soluble liquid aerosol, or solid aerosol can be potentially absorbed. Foam scrubbing is expected to be applicable to any water soluble or water reactive gas, including ammonia, chlorine, ethylene oxide, hydrogen chloride, methyl isocyanate, phosgene, and others; plus particulates and aerosols. Compounds that contain inherently toxic metals such as mercury, cadmium, and chromium will require special attention to ensure that the collapsed foam is collected and properly disposed of. It was determined that 24 gases, 92 liquids, and 163 solids, or a total of 279 compounds (69% of the EHS list) are good candidates for absorption. Of these, 51 compounds (18% of the list) contain metals and would require careful collection and processing of the collapsed foam.

Researchers have successfully absorbed numerous gases in foam, including carbon dioxide, hydrogen sulfide, formaldehyde, acetaldehyde, and mercaptans. Researchers also have reported success with particulates and aerosols, including fly ash, wax, iron oxide, cigarette smoke, ammonium chloride, sulfuric acid mist, propylene glycol, dioctyl phthalate, etc.

Foam is a coarse dispersion of gas in a relatively small amount of liquid (9). The ratio of foam volume to the volume of liquid characterizes the foam and is termed "expansion ratio." Typical expansion ratios for medium expansion foams are between 20:1 and 200:1, and for high expansion foams are greater than 200:1 but usually less than 1000:1 (10). Foam scrubbing can be accomplished with both medium and high expansion foams. It can thus be inferred that from 20 to 1000 volumes of gas can be treated per unit volume of liquid.

Foams have very large liquid surface areas, typically in the range of 1000 to more than 2500 m^2/m^3 (11). Because of these large areas, foam is always thermodynamically unstable; all aqueous foams will collapse eventually. In the fire-fighting and hazardous materials sectors, medium and high expansion foams are characterized by the "quarter drainage time," i.e., the time needed for 25% of the original liquid to drain away. For typical commercially available products, this time ranges from 1 to 14 minutes (1).

Foam generally cannot be formed from pure liquids; a component must always be present to lower surface tension and impart elasticity to the liquid (5, 6, 9). In theory, this component can be a surfactant, a finely divided solid, an insoluble monolayer, or a liquid crystal; however, in practice most foams are surfactant-based.

The presence of surfactant at the air/liquid interfaces in foam may have an effect on absorption performance (12). Most researchers to date have found some inhibition of absorption, although some have found an improvement. However the very high surface area tends to counteract the effects of any inhibition. Additionally, only a fraction of the wide array of available surfactants have been tested (12), and virtually none of the commercial foam formulations have been evaluated. It is thought by one expert in the field (S. Gross, personal communication, 1988) that absorption could be enhanced by careful selection of the foam formulation components.

As noted above, as the foam ages, liquid drains from it. There are two basic types of foam, corresponding to different stages in the drainage process. The first, spherical bubble foam or "kugalschaum" is shown in Figure 4A and consists of bubbles widely separated by liquid. The bubbles exert little influence on one another, and drainage, under the force of gravity, is relatively uniform. As the liquid departs, the bubbles approach one another and are distorted into the polyhedral shapes of the second type, shown in Figures 4B and 4C. Drainage becomes influenced by capillary forces as well as by gravity, and is soon confined to the narrow channels, or "Plateau boundaries," where bubbles meet. Plateau's law states that exactly three bubbles meet at an edge, and exactly four bubbles meet at a point (9, 13).

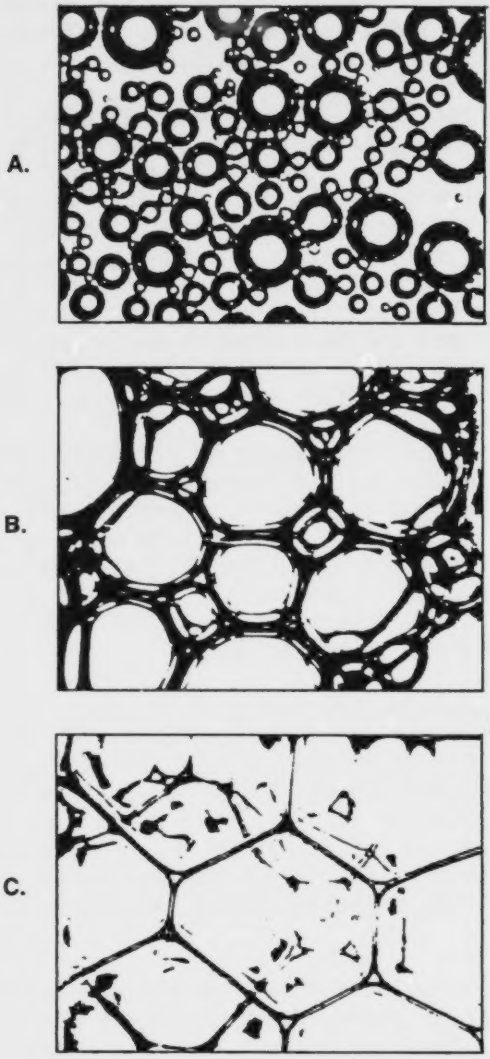
In a medium or high expansion foam, which is polyhedral from the start, most of the liquid is expected to drain through the Plateau boundaries. The significance in terms of scrubbing is that it is not possible to replenish the liquid films by adding liquid to the top of the foam mass; any added liquid would tend to flow through the channels without affecting the main absorbing surfaces. Thus, for all practical purposes, the foam must be thought of as a single-stage system, with finite quantities of gas and liquid in contact for the length of time needed to reach equilibrium.

Medium and high expansion foams are typically produced by spraying the foam liquid (concentrate) against a screen or perforated plate through which air is either blown or aspirated. Figure 5 shows a schematic of typical devices (10). Figure 5A shows a generator in which the air is aspirated by the force of the liquid, while 5B and 5C show generators in which fans provide the air flow. The expansion ratio can be varied by controlling the water flow, the air velocity, and the screen mesh size (7). (Ambient air parameters--temperature, relative humidity--do affect the expansion ratio, and their impact must be taken into account.)

A second device for producing medium or high expansion foam is the flooded plate generator, in which air is blown upward through a perforated plate flooded with foam solution. These generators can foam semiviscous solutions, and also may permit less gas to bypass without forming foam.

Bubble size is an important parameter for scrubbing performance, since it defines the distance that a gas molecule or a particle must travel before reaching a liquid film. For example, the theoretical collection efficiency of 0.05-micron particulate is 50% per second in a 0.5-mm bubble, but only 5% per second in a 10-mm bubble (14).

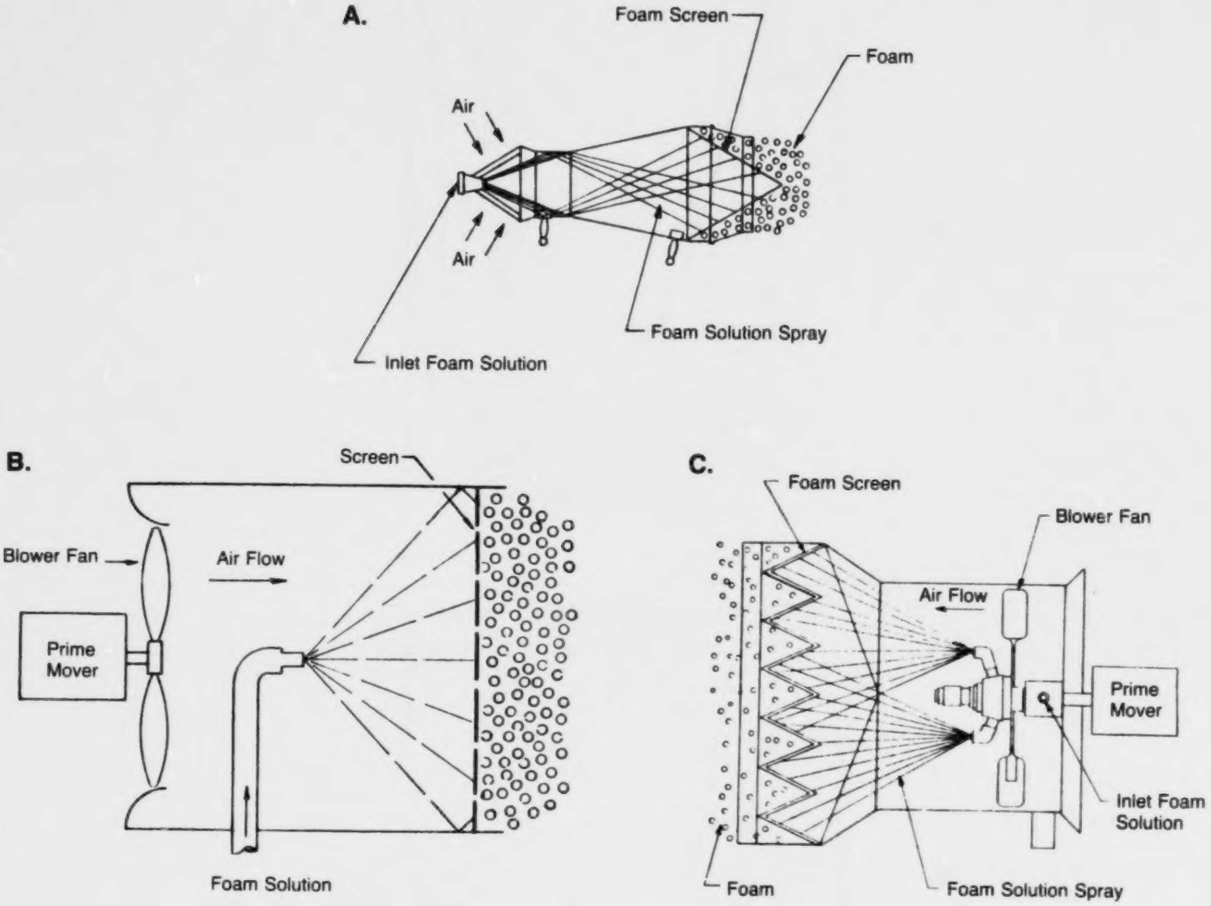
Figure 6 shows the theoretical collection efficiency of particles of various sizes in various sized bubbles. The figure shows high efficiencies for very small particles (by diffusion) and for relatively large particles (by sedimentation). Particles between these sizes are less efficiently collected. This phenomenon is not unique to foam scrubbers and can be counteracted by



Photomicrographs of a spherical bubble foam (**A**), a partially drained polyhedral foam (**B**), and a polyhedral foam with clearly developed lamellae (**C**).

Source: Gillberg, 1980

Figure 4. Photomicrographs of typical spherical and polyhedral bubble foams.
Reprinted with permission from Gillberg, G. Foaming technology--An overview. Hoechst Celanese, 1980.


A.
Foam Screen
Foam
Air
Air
Foam Solution Spray
Inlet Foam Solution
B.
Screen
Blower Fan
Air Flow
Prime Mover
Foam Solution
C.
Foam Screen
Blower Fan
Air Flow
Prime Mover
Inlet Foam Solution
Foam
Foam Solution Spray

A: Aspirating Type Foam Generator. **B** and **C:** Blower Type Foam Generators.

Figure 5. Typical high expansion foam generators. Reprinted with permission from NFPA 11A, Medium and High Expansion Foam Systems, Copyright 1983, National Fire Protection Association, Quincy, MA 02269. This reprinted material is not the complete and official position of the NFPA on the referenced subject which is represented only by the standard in its entirety.

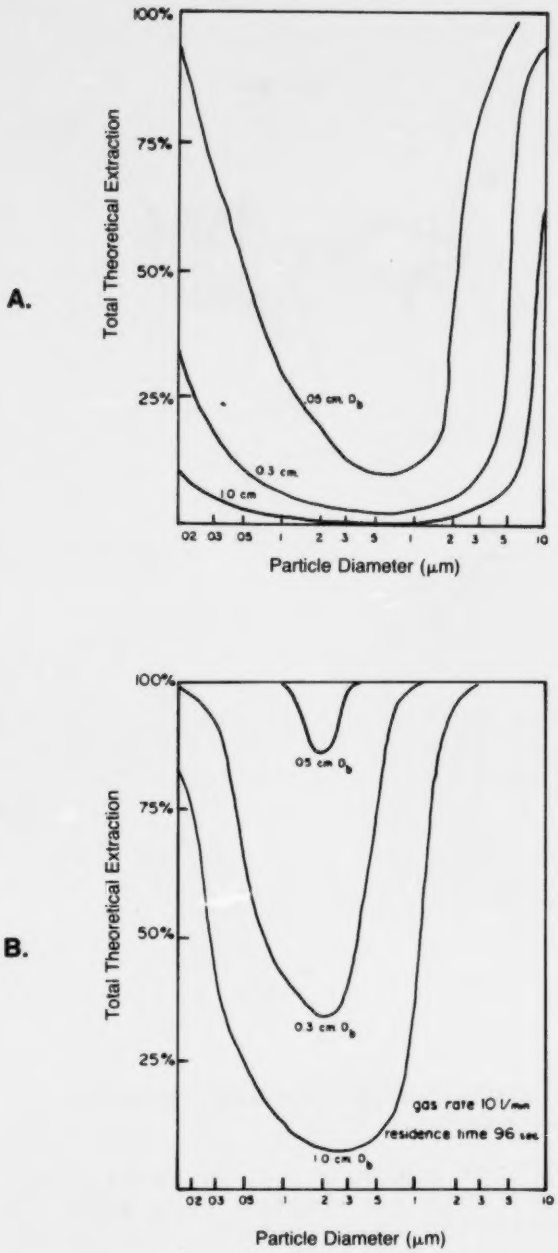


Figure 6. Theoretical particulate collection efficiencies in foam bubbles.
Reprinted with permission from Kaldor, T. and Phillips, C. Aerosol scrubbing by foam. Ind. Eng. Chem., Process Des. Dev., 15(1), Copyright 1976 American Chemical Society.

using longer residence times.

Bubble size can be controlled in a screen-type foam generator by varying the water flowrate, air velocity, surfactant concentration, and screen mesh size (2). The strongest influence is that of screen mesh size, with smaller openings causing an essentially linear decrease in bubble diameter.

The behavior of foam under a range of ambient conditions is also important. When it is used for toxic gas control during an emergency, it is likely that the foam will be piled in some convenient location at the plant or emergency site to allow sufficient residence time for the neutralization to complete. Wind, rain, and temperature extremes can all exaggerate the rate of foam collapse but usually will not fatally impair its effectiveness.

- Temperature: Either hot and dry or very cold conditions can cause difficulties. Freezing can occur at temperatures below the freezing point of water. The effect is most noticeable when the cold air is external to the foam, because of the formation of a frozen crust.

  Hot, dry conditions can cause evaporation from the foam pile, especially when accompanied by wind. Evaporation, together with the normally-occurring drainage, increases the rate of water loss and bubble rupture.

- Wind: Wind accelerates the rate of evaporation from the foam mass. In winds over 10-15 mph, some form of containment is necessary; chunks of foam may blow away. According to MSA Research Corp. (7), chain link fence can be used for foam depths of 2-3 ft, and hardware cloth or netting for greater depths.

  Other manufacturers mention storm fencing, mosquito netting (National Foam), and polyethylene tubes (Rockwood Systems "Macrobar" system). Rockwood indicates that not only can the tubes, which are 8 ft in diameter and 100-200 ft long, be filled with foam, but they can also be arranged to form an enclosure for more foam.

  At many chemical plants there may be existing structures (such as diked areas around tanks, sheltered areas between buildings, warehouses, etc.) that could be used for foam containment on an emergency basis. Finally, it should be noted that although stronger winds may cause difficulty for foam usage, they would also improve the dispersion of any released chemical, usually lessening the overall hazard.

- Rain: Rain also accelerates the rate of collapse, typically by approximately 30%. Most foam manufacturers have test data for the performance of their products when water sprinklers are used simultaneously with the foam.

PREVIOUS RELEVANT RESEARCH

A number of researchers previously have studied the absorption of gases, vapors, particulates, and/or aerosols into foams. A literature search (both manual and computerized) was conducted to locate such previous work. In many cases, the studies are of limited usefulness because: (1) the focus of the research is different from that of the current work, (2) different parameters are emphasized or key parameters are not reported, or (3) conditions used are dissimilar to those anticipated in the current work.

However, in general, the results of previous work have shown success in the removal of contaminants into foam. Studies in which reagents were incorporated into the foam liquid for removal of reactive gases generally were able both to produce stable foams incorporating the reagent and to neutralize the absorbed gas by this means.

Thus, overall, the results of previous work can be viewed as encouraging in regard to the potential success of foam scrubbing as applied to emergency control of toxic releases. There is, however, a need for clearly defined and described experimental work to answer many remaining questions.

GAS ABSORPTION STUDIES

Table 1 provides an overview of studies that have been done on absorption of gases into foams.

Several researchers (11, 15, 16) worked with mass transfer of CO_2. Biswas (16) and Shah (11) added reagents (i.e., NaOH, Na_2CO_3) to neutralize the absorbed gas. Results reported included: a) influence of surfactant on mass transfer coefficient and b) overall mass transfer comparable to that in conventional packed columns.

Absorption of several reactive gases was studied (17), namely, hydrogen sulfide, formaldehyde, acetaldehyde, and propionaldehyde into very low expansion foam (expansion ratio 4 to 6) in an upflow column.

The gas concentrations used ranged from 0.017 to 0.36 % (v/v). A total of nine different surfactants were tested with varying surfactant concentrations. No major influence of surfactant type or concentration was found. Pollutant removals were found to be very good. Efficiencies of 80% to 99% were reported for formaldehyde and 74% to 99% for acetaldehyde, in residence times of 1.75 to 3.5 seconds.

In further experiments, reagents were added to the foam: $Na_2S_2O_5$ to the runs for formaldehyde and acetaldehyde, and $CuSO_4$ for hydrogen sulfide. Efficiencies for both formaldehyde and acetaldehyde were improved to better than 99% in the presence of the additives, and efficiencies of better than 90% were achieved for hydrogen sulfide.

Gillberg (5) briefly summarized several additional studies:

> "Nitrous oxides have been removed with high efficiency from air by reactive foam containing urea or sodium hydroxide. Reactive iodine-containing gases might be released from nuclear power stations at an accident. Studies have shown that reactive foams can be very effective. Poignant gases such as mercaptans and hydrogen sulfide

TABLE 1. SUMMARY OF PREVIOUS WORK ON GAS SCRUBBING USING FOAM

Study	Gaseous Contaminant		Surfactant		Reagent	Bubble Size	Expansion Ratio	Results
	Type	Concentration	Type	Amount				
Metzner, 1956	CO_2(1)	Sat'd(1)	"Detergent": Nacconal and Glim	Varied: 0 to 0.33%	None	1-5 mm	Varied: 1.03 to 1.6	Mass transfer found comparable to conventional packed column.
Jackson, 1963(2)	Varied: NH_3 N_2O_3 SO_2 CO_2	Varied	NR(3)	NR	Varied: NaCl H_2SO_4 NH_3	NR	NR	Absorption rate coefficients from 7 to 260 times higher than conventional equip't
Biswas, 1981	CO_2	0.4-0.5%	NR	NR	NaOH	NR	Varied:(4) 20 to 35	Mass transfer agreed with polyhedral model
Shah, 1984	CO_2	10 vol%	HDTMAB Triton X-100	0.5 wt% 1 vol%	NaOH $Na_2CO_3/NaHCO_3$	2.2 to 5.4 mm	Varied: 20 to 500	Mass transfer higher than packed beds for slow rxn; lower for fast rxn.
Brander, 1984	H_2S HCHO CH_3CHO CH_3CH_2CHO	Varied: 0.017 to 0.36 vol%	Varied(5)	Varied	$CuSO_4$ $Na_2S_2O_5$	NR	4-6	Very good removal in 1.75 to 3.5 sec: HCHO: 80% to >99% CH_3CHO: 74% to >99% H_2S: >90%

(continued)

TABLE 1. (continued)

Study	Gaseous Contaminant		Surfactant		Reagent	Bubble Size	Expansion Ratio	Results
	Type	Concentration	Type	Amount				
Gillberg, 1980$^{(2)}$	a. Nitrous gases	NR	NR	NR	Urea NaOH	NR	NR	High efficiency
	b. Mercaptans H_2S	NR	NR	NR	Cu(II) Salts or pH>10.7	NR	NR	Effectively removed
Ohkawa, 1987 [18]	O_2	NR	NR	NR	None	3.5mm avg	NR	Mass transfer coefficients ranged from 9×10^{-5} to 2×10^{-4} m/sec

Notes:
(1) The surfactant solution was saturated with CO_2 before foaming. The authors measured rate of desorption of CO_2 into foam.
(2) Review of other research work.
(3) NR - Not reported
(4) Calculated as inverse of volume fraction liquid (for newly generated foam).
(5) See text for details.

> are very effectively removed (>98%) by reactive foams containing copper (II) salts or highly alkaline (pH>10.7) foams. The use of foams to remove formaldehyde from air streams also looks very promising."

FOAM SCRUBBING OF PARTICULATES AND AEROSOLS

Table 2 presents an overview of studies that have been done on collection of particulates and aerosols into foam.

Researchers have studied absorption of particles of various sizes into a range of bubble sizes. In some of the studies, different surfactants were compared, and wettable vs. nonwettable particulates were evaluated.

Damle (19) studied absorption of resolidified wax droplets, ranging from 0.1 to 5.0 microns in size. Some runs were made with hydrophillic methylene blue for comparison.

Three surfactants were used, namely, hexadecyltrimethylammonium bromide (cationic), sodium oleate (anionic), and Triton (nonionic). A range of bubble sizes were studied, from 0.8 mm to 5.3 mm, by varying the size of the wire mesh distributor.

Results show that collection efficiency increases for longer residence times and for smaller bubble sizes. For a bubble size of 0.8 mm, the particle removal was in the range of 80% to nearly 100% for a residence time of 90 sec.

Collection efficiency was found to be at a minimum in the 0.2 to 0.4-micron particle-diameter range. This was found to occur due to a change in the dominant collection mechanism from diffusion for small particles to sedimentation for larger particles.

The two ionic surfactants were found to perform somewhat better than the nonionic type. Finally, the hydrophillic methylene blue aerosol was found to be collected more readily (up to 20% to 30% higher efficiency) than the wax particulate.

VAPOR SUPPRESSION FROM LIQUID POOLS

A number of studies have been made of a related area of foam use, namely, application for suppression of vapors from liquid pools of spilled chemicals. In that application, the main purpose of the foam is to prevent or minimize evaporation from the liquid. However, vapors that do escape are scrubbed to some extent as they rise through the foam blanket. Vapors from cryogenic gases (such as NH_3) are also warmed by travel through foam, improving dispersion (1).

The scrubbing that occurs in a foam blanket over liquid is different from scrubbing, in which the contaminated air is used to blow the bubbles. In a foam blanket, the air within the bubbles is initially clean. Scrubbing occurs as pockets of vapor make their way upward, either forming new bubbles, channeling, or diffusing through the existing foam.

TABLE 2. SUMMARY OF PREVIOUS WORK ON PARTICULATE AND AEROSOL SCRUBBING USING FOAM

Study	Particulate/Aerosol		Surfactant		Bubble Size	Results
	Type	Size	Type	Amount		
Bransky & Diwoky, 1940 (1)	H_2SO_4 fog	NR(2)	NR	NR	NR	>90% in > 10 sec
Yano et al, 1955 (1)	Ammonium chloride Cigarette smoke H_2SO_4 mist	~0.1um	NR	NR	2-7 mm	~100% in 90 sec
Pozin et al, 1954-1956 (1)	"Dust"	2-30 um	NR	0-0.1 %	NR	"Good" for >5 um size Surfactant improved efficiency
Jackson, 1963 (1)	NR	NR	NA	0 %	NR	Confirmed above findings
Taheri, 1968 (1)	NR	< 3 um	NR	0-NR	NR	50% for 3 um 10% for < 1 um Surfactant decreased efficiency
Silverman, 1962 (1)	Uranine	0.072 um 0.02 um	NR	NR	~1 cm	95% in 160 sec
Browning & Ackley, 1962 (1)	Iodine	0.0065 um 0.0014 um	NR	NR	NR	95% in less time than above
Surati, 1975 (1) Limaye, 1976	Polystyrene latex	0.18 um 0.8 um	varied	NR	NR	> 90% in 3-4 sec Surfactant type showed little effect
Kaldor, 1976	Fly ash	1.3 um avg	Note (3)	0.3 g/l	3 mm Avg.	High efficiency on >2 um particles. Aggregation suspected.

(continued)

TABLE 2. (continued)

Study	Particulate/Aerosol		Surfactant		Bubble Size	Results
	Type	Size	Type	Amount		
Ctvrtnicek, 1976	Dioctyphthalate Polypropylene glycol	0.18-1.0 um	Tergitol TMN Aerosol OT Sterox	2%	0.8 mm 3.9 mm	Dioctyl phthlate:~95% in 80 sec. Polypropylene glycol: ~75% in 80 sec.
Ctvrtnicek, 1977(4)	Fly ash	0.056-1.0 um	Tergitol	0.25 wt%	3 mm est	50% to 75% in 20 sec; better efficiency for the smallest particles
Ramsey, 1977 [20]	Fe_2O_3	0.2-10 um	Tergitol	NR	1.0 mm	95% in 2 minutes
Damle, 1980	Wax Methylene blue	0.1-5.0 um	HDTMAB(5) Sodium Oleate Triton	0.5 wt % 0.5 wt % 1.0 vol %	Varied: 0.8mm to 5.3 mm	<0.4 um: 70% in 90 sec 0.56-1.0 um: 90% for wax >2 um: 100%, 0.8 mm bubbles

Notes:
(1) As reported by Damle, 1980
(2) NR - Not reported
(3) Ethylhexadecyldimethylammonium bromide
(4) 500 cfm pilot scrubber
(5) Hexadecyltrimethylammonium bromide

Liquid pool suppression studies have established important data on the compatibilities and interactions of various gases with different foam types. The information from these studies is readily available in the literature (1, 3,21-26) and is therefore not reiterated here.

COMPARISON TO ALTERNATIVE TECHNIQUES

There are currently a variety of techniques available to prevent, control, or mitigate hazardous accidental releases of air toxics (EHSs). Preventive techniques include, for example, alarms and interlocks that allow corrective action to be taken before a release occurs. Control measures include scrubbers, flares, and other devices intended to capture and destroy escaping contaminants before a release can occur. Finally, if a release does occur, mitigative measures such as water curtains can be used to reduce the off-site impact.

Foam scrubbing falls into the categories of control and mitigation. A foam generator can be used in the same manner as a scrubber to protect against releases from process equipment or buildings; or it can be used to draw in a gas cloud from, for example, a leaking pipeline or vessel. (Strategic positioning of "at ready" units must be considered.)

In the first case, the advantages of the foam generator are:

- Equipment is relatively small and can be on standby until needed.
- Large volumes of gas can be controlled with relatively small amounts of liquid.
- Residence time can be provided within the foam mass, rather than requiring a large, permanent vessel.
- The foam generator can be readily sized for a large emergency flow (i.e., up to 30,000 cfm per unit).

Techniques currently used for mitigation of vapor clouds include water sprays and curtains, steam curtains, and air curtains. Where liquid is also present, techniques include dilution, neutralization, temporary covering, freezing, and ignition (27, 28).

The water, steam, and air curtain techniques are primarily used to disperse the released gases and have been shown to reduce concentrations by a factor of from 1.5 to 4, depending on wind speed (27). Some scrubbing is also provided by water curtains, but only when very large water volumes are used. In tests with hydroflouric acid, up to 50% scrubbing was found (R. Hiltz, personal communication, 1987). The main disadvantages of these techniques are: 1) their relatively low effectiveness, and 2) the high levels of plant utilities required.

Based on the foam scrubbing efficiencies measured by previous researchers, it is felt that this technique can provide better mitigation, in many cases, than the currently available alternative techniques.

EXPERIMENTAL WORK

To date, a set of preliminary tests has been carried out to qualitatively establish the effectiveness of foam scrubbing. In these tests, smoke from SAFE-VUE^{TM} colored smoke candles--a dispersion of airborne dye particles--was ducted into an MSA Fast Response^{TM} high expansion foam generator using MSA Fast Response^{TM} high stability foam concentrate at the manufacturer's recommended concentration. The Fast Response^{TM} generator produces approximately 225:1 expansion foam at a rate of approximately 35 cfm. Observation of the foam leaving the nozzle showed that essentially all of the smoke was incorporated into the foam; no escaping smoke was seen.

The foam persisted for several minutes or more when piled on the ground. No smoke was seen to escape from the collapsing (draining) foam pile, and the foam took on the color of the smoke. Closer observation showed the color to be present in the liquid lamellae of the foam bubbles.

These preliminary results are very encouraging. More detailed testing is planned, on both laboratory and demonstration scales, to quantify the effectiveness of foam scrubbing on hazardous materials.

CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE WORK

This study indicates that utilization of foam systems is a viable and potentially cost-effective method for the capture and neutralization of large volumes of released toxic vapors. There is certainly a need for the emergency control capability that could be achieved using foam technology.

The results of previous work with foam are encouraging, showing generally good absorption efficiency for both gases and particulates. There is, however, a need for clearly defined and described experimental work to bring the foam concept to an industrial reality.

Therefore, we believe that foam technology could be a valuable addition to the range of available techniques.

It is strongly recommended that a program of laboratory testing followed by demonstration at pilot plant scale be carried out. It is expected that this testing program will allow foam technology to develop rapidly from a concept into a viable control option.

REFERENCES

1. Gross, S.S., and Hiltz, R.H. Evaluation of foams for mitigating air pollution from hazardous spills. EPA-600/2-82-029. U.S. Environmental Protection Agency, 1982, 73 pp.

2. Ctvrtnicek. Monsanto Research Corporation. Application of foam scrubbing to fine particle control, Phase I and Phase II. EPA-600/2-76-125. U.S. Environmental Protection Agency. 1976. 213 pp.

3. Hiltz, R.H. Mitigation of the vapor hazard from silicon tetrachloride using water-based foams. J. Hazardous Materials. 5, 1982.

4. Jackson, J. Gas cleaning by the foam method. British Chemical Engineering. 8:5, 1963.

5. Gillberg, G. Foaming technology - An overview. In: Proceedings of the Eighth Technical Symposium: Nonwovens - Innovative Fabrics for the Future. 1980.

6. Kouloheris, A.P. Foam: friend and foe. Chemical Engineering, 1987.

7. MSA Research Corporation. Information Package on Fire Protection Systems and Components. Evans City, Pennsylvania, 1986.

8. Federal Register, April 22, 1987, pp 13403-13410

9. Ross, S. Foams. In: Kirk-Othmer Encyclopedia of Chemical Technology. Vol.11, 1983. pp. 127-145.

10. National Fire Prevention Assoc. Standard for Medium and High Expansion Foams. Philadelphia, Pennsylvania, 1983.

11. Shah, P.S. and Mahalingam, R. Mass transfer with chemical reaction in liquid foam reactors. AIChE Journal. 30:6, 1984.

12. Nguyen Ly, L.A., et. al. Diffusion of gases through surfactant films: Interfacial resistance to mass transfer. AIChE Journal. 25:6, 1979, pp. 1015-1024.

13. Ross, S. Bubbles and foam. Industrial and Engineering Chemistry. 61:10, 1969.

14. Kaldor, T.G. and Phillips, C.R. Aerosol scrubbing by foam. Ind. Eng. Chem. Process Des. Dev. 15:1, 1976. pp. 199-206.

15. Metzner, A.B., et. al. Mass transfer in foams. Industrial and Engineering Chemistry. 48:11, 1956. pp. 2040-2045.

16. Biswas, J. and Kumar, R. Mass transfer with chemical reaction in a foam bed contactor. Chemical Engineering Science. 36:9, 1981.

17. Brander, S.M., et. al. Reactive foams for air purification. Environ. Sci. Technol. 18:4, 1984.

18. Ohkawa, A., et. al. Bubble size, interfacial area, and volumetric liquid - phase mass transfer coefficient in downflow bubble columns with gas entrainment by a liquid jet. Journal of Chemical Engineering of Japan. 20:1, 1987.

19. Damle, A.S. Gas submicron particulate separation in a flowing liquid foam bubble matrix. PhD Dissertation. Wash. State Univ. Pullman, Washington, 1980.

20. Ramsey, G.H. Evaluation of foam scrubbing as a method for collecting fine particulate. EPA-600/2-77-197, U.S. Environmental Protection Agency, 1977 33 pp.

21. Greer, J.S., Gross, S.S., Hiltz, R.H., et. al. Modification of spill factors affecting air pollution. Vol 2. The Control of the Vapor Hazard from Spills of Liquid Rocket Fuels. EPA-600/2-81-215. U.S. Environmental Protection Agency, Cincinnati, Ohio, 1981.

22. Takimoto, H.H., Lewis, S., and Hiltz, R. Vapor suppressant foam systems for propellant spills. In: Proceedings of the 1984 Hazardous Material Spills Conference. Nashville, Tennessee, 1984.

23. Evans, M.A., and Carroll, H.A. Handbook for Using Foams to Control Vapors from Hazardous Spills. Contract 68-03-3113, U.S. Environmental Protection Agency 1985, 26 pp.

24. Hiltz, R.H. Control of the vapor hazard from reactive volatile hazardous materials by foam. In: Proceedings of First Technical Seminar on Chemical Spills. 1983. pp. 63-74.

25. Norman, E.C. and Dowell, H.A., National Foam Systems, Inc. Using aqueous foams to lessen vaporization from hazardous chemical spills. Chemical Engineering Progress, Technical Manual on "Loss Prevention," Vol. 13, 1980, 7 pp.

26. Norman, E.C. Vapor mitigation by the use of foam: Case history and large-scale outdoor tests. In: Proceedings of the Hazardous Materials Spills Conference, 1982.

27. Brown, L.E., et. al. Hazard control methods for high volatility chemicals. In: Proceedings of the International Symposium on Preventing Major Chemical Accidents. Center for Chemical Process Safety of the American Institute of Chemical Engineers. 1987.

28. Prugh, 1987. Post-release mitigation design for mitigation of releases. In: Proceedings of the International Symposium on Preventing Major Chemical Accidents. Center for Chemical Process Safety of the American Institute of Chemical Engineers. 1987.

TRANSPORT OF INORGANIC COMPOUNDS THROUGH COMPACTED CLAY SOIL

by: David E. Daniel
University of Texas
Austin, Texas 78712

Charles D. Shackelford
Colorado State University
Ft. Collins, Colorado 80523

Wing-Ping Liao
University of Texas
Austin, Texas 78712

ABSTRACT

The simplest approach to prediction of the rate of transport of solutes through compacted clay soil is to compute the seepage velocity of the transporting liquid based on the hydraulic conductivity of the soil, the hydraulic gradient, and the effective porosity of the soil. However, such analyses fail to account for mechanical dispersion and molecular diffusion. With compacted clay soils having low hydraulic conductivity, molecular diffusion is an important mechanism of chemical transport at the low hydraulic gradients that typify field values.

The purpose of this research was to study experimentally the migration of inorganic solutes through compacted clay soil at realistic hydraulic gradients. A major portion of the research focused on molecular diffusion. It was found that the diffusion coefficient for compacted clay soil was insensitive to the geomechanical factors that were studied (such as molding water content and method of compaction) but was very sensitive to geochemical factors. Typical data are used to demonstrate that: (1) clay liners release contaminants primarily by molecular diffusion if the hydraulic conductivity is on the order of 10^{-8} to 10^{-9} cm/s or less, and (2) breakthrough of contaminants can occur much sooner than predicted by models that ignore diffusion.

INTRODUCTION

Compacted soil liners are a vital component of nearly all solid waste disposal facilities and surface impoundments for hazardous waste. Soil liners are intended to slow the release of contaminants and to retard the migration of many of the dissolved contaminants that enter the liner (1). Predictions of the performance of soil liners center on the volume, Q, of liquid that will leak through a liner with an area A and a hydraulic conductivity k over a period of time t, when the hydraulic gradient driving flow is i. Based on Darcy's law:

$$Q = k\,i\,A\,t \tag{1}$$

More sophisticated analyses of the release of contaminants through a soil liner are needed to account for the movement of solutes. In general, two mechanisms are responsible for the migration of solutes in leachate through a soil liner: (A) advective transport, which is the transport of solutes by flowing water in the soil, and (B) molecular diffusion, which is the transport of solutes by thermal-kinetic energy gradients, or gradients in the concentration of a solute (2). For soil liners with low hydraulic conductivity, molecular diffusion can be a significant mode of transport of solutes through soil liners (3-7).

The desired prediction for leachate migrating through a clay liner is the temporal variation of the concentration (c) of one or more solutes in the material underlying the soil liner (Fig. 1). Graphs such as the one shown in Fig. 1 are called "breakthrough curves." Breakthrough curves can be measured in the laboratory by permeating soil with liquid having a known and constant concentration (c_o) of a particular solute and measuring the concentration (c) of the solute in the effluent reservoir over time. Breakthrough curves are often plotted in a slightly different form; the abscissa is typically pore volumes of flow (P), which is the cumulative quantity of inflow divided by the volume of the void space in the soil, and the ordinate is the relative concentration, c/c_o. Several such curves are shown in Fig. 2. In Fig. 2, "retardation" refers to the slowing of solute movement as a result of ion exchange, precipitation, or other geochemical reactions.

In soil, pores of various sizes and degrees of connectivity exist. Some pores may be relatively ineffective in conducting flow whereas other pores (especially large pores, cracks, or fissures) may conduct a relatively large percentage of the flow. The "effective porosity" is a measure of the volume occupied by the pores that conduct most of the flow divided by the total volume of the soil (2). If all the pores conduct flow equally well, then the effective porosity (n_e) will equal the total porosity (n). In compacted clay soil, there is evidence that n_e/n can be much less than one (8), indicating that a small percentage of the pores (the largest ones) conduct most of the flow. The effective porosity may be determined from a breakthrough curve; n_e is the pore volumes of flow at $c/c_o = 0.5$ (9). Except when large advective velocities mask the effects of diffusion, such determinations of n_e are not correct because they fail to account for the influence of molecular diffusion upon the transport of solutes through a soil column. Diffusion may cause breakthrough at less than one pore volume of flow even if all pores are equally efficient conductors.

MOLECULAR DIFFUSION

BACKGROUND

The process of diffusion is usually assumed to occur in accord with Fick's first and second laws. For free solutions (i.e., no porous matrix), Fick's first law states that one-dimensional diffusion occurs as follows:

$$J_d = -D_o \frac{\partial c}{\partial x} \tag{2}$$

where J_d is the diffusional mass flux (mass transported per unit area perpendicular to the direction of transport, per unit time), D_o is the free-solution diffusion coefficient, c is the concentration of a solute, and x is the direction in which the diffusion is occurring.

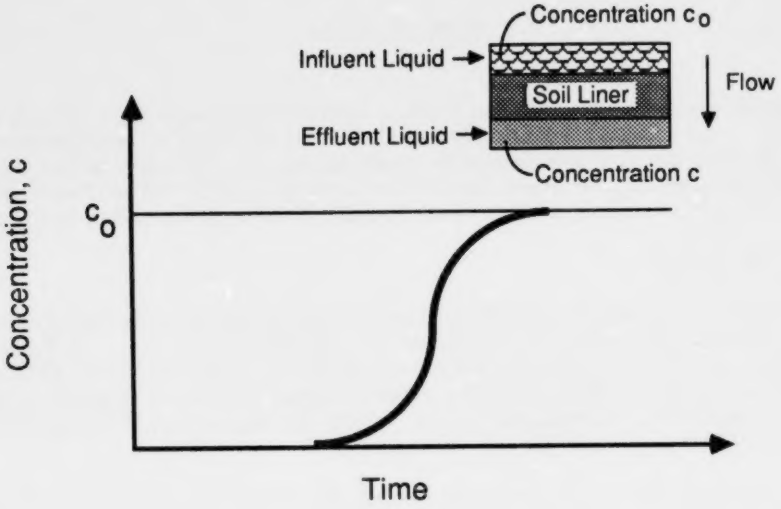
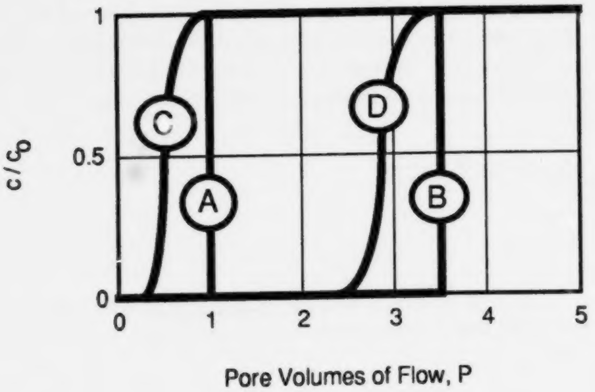

Concentration c_o
Influent Liquid
Soil Liner
Flow
Effluent Liquid
Concentration c
Concentration, c
c_o
Time

Figure 1. Breakthrough curve for column test.



Curve	Diffusion/ Dispersion?	Retardation?
A	No	No
B	No	Yes
C	Yes	No
D	Yes	Yes

Figure 2. Breakthrough curves for various conditions.

Solutes will not diffuse as quickly in soil as they will in free solutions. For soil, Eq. 2 becomes

$$J_d = -\left(\tau D_o\right)\theta \frac{\partial c}{\partial x} \tag{3}$$

or

$$J_d = -D^*\theta \frac{\partial c}{\partial x} \tag{4}$$

where τ is a dimensionless tortuosity factor, θ is the volumetric moisture content of the soil, and D^* is the effective diffusion coefficient. It should be noted that some researchers include θ in the tortuosity factor. The tortuosity factor accounts for the increased distance of flow and the more tortuous pathways experienced by solutes diffusing through soil. In reality, there may be other effects associated with the tortuosity factor, e.g., the variation in the viscosity of the solvent within the pore space and the negative adsorption (exclusion) of ions (10).

Fick's first law describes steady-state flux of solutes. For unsteady (transient) transport, Fick's second law applies:

$$\frac{\partial c}{\partial t} = D^* \frac{\partial^2 c}{\partial x^2} \tag{5}$$

Equation 5 is integrated for appropriate initial and boundary conditions to obtain a description of the solute concentration changes with respect to time and space. Complementary error functions facilitate the integration.

EXAMPLE

An example of the application of Fick's second law is as follows. A 1-m-thick clay liner retains leachate containing a particular solute at a concentration of 10,000 mg/L. The underlying ground water is completely free of this solute. The effective diffusion coefficient is assumed to be 2×10^{-10} m^2/s. The resulting distribution of solute in and at the bottom of the liner as a function of time is illustrated in Fig. 3. The solute distribution was determined from the following solution to Eq. 5 (11), which assumes the leachate concentration is constant with time:

$$\frac{c}{c_o} = \mathrm{erfc}\left(\frac{x}{2\sqrt{D^* t}}\right) \tag{6}$$

where erfc is the complementary error function. The concentrations of solute reaching the base of the liner at 10, 20, 40, and 80 years are approximately 50, 460, 160, and 3200 mg/L, respectively. As illustrated in this example of chemical transport through a liner by diffusion alone, the diffusion of chemicals through fine-grained materials can be an important transport mechanism even over relatively short (10 - 30 years) periods.

EXPERIMENTAL PROGRAM

The apparatus shown schematically in Fig. 4 was used to measure the diffusion coefficient of compacted clay soils (12). Kaolinite, which is a commercially-produced material, and Lufkin clay, which is a naturally-occurring soil rich in smectite, were used in the experiments. Data on the soils are given in Table 1.

Test specimens were compacted, soaked in 0.01 N $CaSO_4$ until advective flow ceased, and then exposed on one side to a simulated waste liquid containing three anions (Cl^-, Br^-, and I^-) and three cations (K^+, Cd^{2+}, and

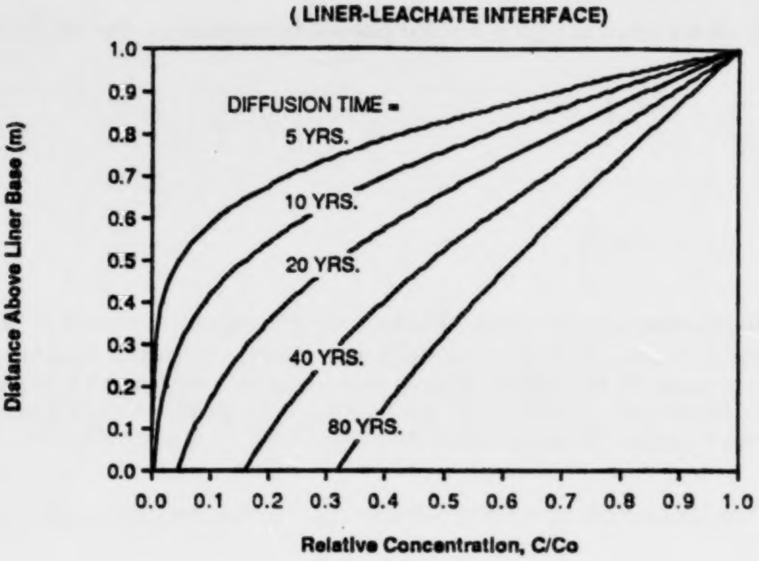


Figure 3. Concentration profiles for 1-m-thick clay liner releasing solute solely by molecular diffusion.

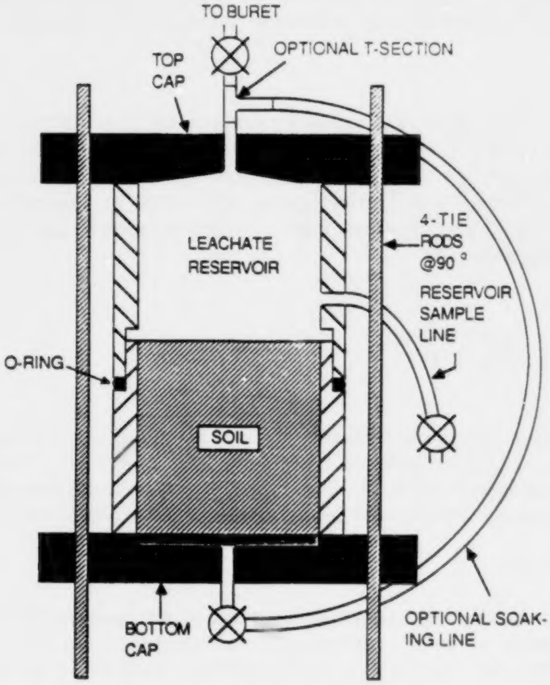

TO BURET
OPTIONAL T-SECTION
TOP CAP
LEACHATE RESERVOIR
4-TIE RODS @90 °
RESERVOIR SAMPLE LINE
O-RING
SOIL
BOTTOM CAP
OPTIONAL SOAK-ING LINE

Figure 4. Schematic drawing of diffusion cell.

TABLE 1. PROPERTIES OF SOIL

Property	Method of Measurement	Value of Property Kaolinite	Lufkin Clay
Natural Water Content (g/g)	ASTM D2216	Dry	23%
Dominant Clay Mineral	X-Ray Diffraction	Kaolinite	Smectite
Optimum Moisture Content (g/g)	ASTM D698	32%	20%
Max. Dry Unit Weight	ASTM D698	83 pcf	102 pcf
Liquid Limit (g/g)	ASTM D4318	54%	56%
Plasticity Index (g/g)	ASTM D4318	23%	42%
Exchangeable Cations (meq/100g)	Ref. 13		
Na^+		3.8	6.4
K^+		0.8	2.7
Ca^{2+}		1.0	19.1

Zn^{2+}) at two concentrations (0.04N and 0.013 N). The soil variables included molding water content and method of compaction. Diffusion coefficients were determined from reservoir concentrations, corrected to ensure mass balance, after several weeks of exposure to the simulated waste liquid. At least two replicates were conducted for each test. Further details are given by Shackelford (12).

RESULTS AND DISCUSSION

The results of the experiments on 0.04 N synthetic leachate are summarized in Table 2. The experiments yielded effective diffusion coefficients generally in the range of 2 - 4 x 10^{-10} m^2/s for anions diffusing in kaolinite and 0.5 to 2 x 10^{-10} m^2/s for anions diffusing in Lufkin clay. The diffusion rates for cations were in some instances markedly lower than for the anions because of ion exchange and possibly other geochemical reactions. However, there was little correlation between adsorption patterns noted in the diffusion tests and those observed in batch-adsorption tests; the much lower soil-solution ratio used in batch adsorption tests relative to column tests on compacted soils is thought to be responsible for the differences noted. Neither molding water content nor method of compaction had much influence on the measured diffusion coefficients. The test data were very sensitive to subtle variations in geochemical factors (such as leachate strength and ion competition) but were insensitive to geophysical parameters (such as molding water content and method of compaction).

ADVECTIVE-DIFFUSIVE TRANSPORT

THEORETICAL BACKGROUND

The advective transport of conservative (non-attenuated) solutes through soil is assumed to occur in accord with Darcy's law. The advective flux (J_a) may be computed with the following equation (12):

$$J_a = c\, n_e\, v_s = -c\, k \frac{\partial h}{\partial x} \tag{7}$$

TABLE 2. RESULTS OF DIFFUSION EXPERIMENTS ON 0.04 N SYNTHETIC LEACHATE

Soil	Compaction	Molding Water Content (%)	Number of Tests	Average Effective Diffusion Coefficient, $D^* \times 10^{10}$ m^2/s					
				Cl^-	Br^-	I^-	K^+	Cd^{2+}	Zn^{2+}
Kaolinite	Std. Proctor	24	3	4.1	2.5	3.0	1.5	1.7	2.1
"	"	27	3	3.9	3.0	1.1	0.9	1.3	1.9
"	"	30	3	3.8	3.3	3.7	1.2	1.3	1.8
"	"	33	3	2.8	2.5	3.6	1.2	1.6	2.0
"	"	36	3	3.6	2.2	2.2	1.6	1.1	2.6
"	Kneading	33	2	3.8	2.2	3.7	1.3	0.7	0.8
"	Static	33	2	3.3	2.2	2.1	0.9	0.3	0.3
Lufkin Clay	Std. Proctor	22	2	1.5	0.7	0.5	0.01	3.0	1.7

where h is the total hydraulic head and the other terms are as defined earlier. Many solutes in leachate will be attenuated by soil, e.g., by ion exchange, sorption by organic carbon, precipitation, oxidation/reduction reactions, and others. The retardation coefficient, R, for a solute may be defined as the number of pore volumes of flow that is needed to achieve $c/c_o = 0.5$, divided by the number of pore volumes needed to achieve $c/c_o = 0.5$ for a conservative tracer, when in both instances the flow is purely advective. Thus, if $n = n_e$, a conservative tracer will break through a soil column ($c/c_o = 0.5$) at 1 pore volume of flow whereas a solute with R = 2 will break through at 2 pore volumes of flow. The idea is illustrated in Fig. 5.

The retardation coefficient may be computed from the following relationship:

$$R = 1 + \frac{\rho_d}{\theta} K_p \qquad (8)$$

where ρ_d is the dry bulk density of the soil, θ is the volumetric water content, and K_p is the partition coefficient, which relates mass of solute sorbed per unit mass of soil to the concentration of solute in solution at equilibrium. Batch adsorption tests are often used to determine K_p (14).

EXPERIMENTAL PROGRAM

The same soils and ions mentioned earlier in the discussion of tests to determine effective diffusion coefficients are being utilized in column experiments with combined advective/diffusive transport. Hydraulic gradients in the range of 1 to 20 are being used for kaolinite, and gradients of 20 and 50 are being used for tests on Lufkin clay. Some test specimens have been soaked with standard solutions prior to permeation, and others have been permeated without presoaking. Tests are still in progress. In general, significant diffusive flow has been seen at the lowest gradients while flow seems to be primarily advective at the higher gradients.

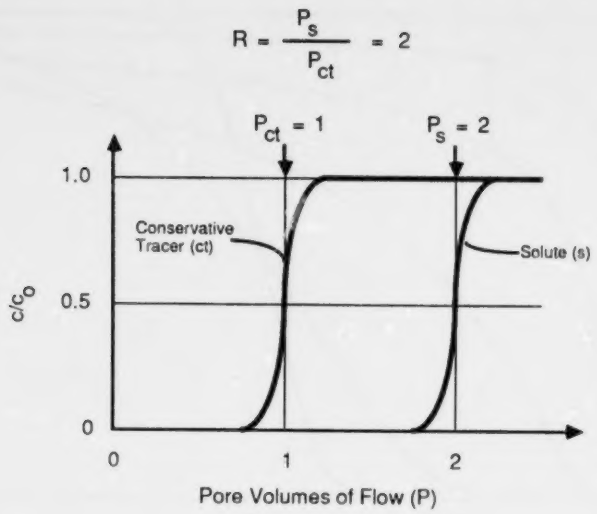


Figure 5. Definition of retardation coefficient (R) for a solute.

RELATIVE IMPORTANCE OF DIFFUSION

The data presented earlier, plus information in the literature (12), indicate that the effective diffusion coefficient for anions diffusing through clay soils covers a fairly narrow range; a value of 2 x 10^{-10} m^2/s may be taken as typical. For landfills with leachate collection systems, the hydraulic gradient is likely to be slightly greater than unity (ignoring suction pressures); a value of 1.3 may be taken as typical. A typical thickness for a clay liner is 3 feet. The breakthrough curves shown in Fig. 6 have been computed for these assumed conditions using the Ogata (15) solution. Without diffusion, all the curves would be the same, but with diffusion, the pore volume at which $c/c_o = 0.5$ is a function of the hydraulic conductivity of the soil. For these conditions, diffusion is relatively unimportant for hydraulic conductivities greater than 1 x 10^{-7} cm/s but becomes important for conductivities of 1 x 10^{-8} cm/s or less.

Another way to view the influence of diffusion is to plot the breakthrough time as a function of the hydraulic conductivity of the soil. This has been done for the conditions outlined in the previous paragraph; the results are shown in Fig. 7. At very low hydraulic conductivities, flow is purely diffusive, and at very high values, flow is entirely advective.

The relative importance of advection and diffusion as mechanisms of contaminant transport through clay liners may also be evaluated in terms of mass fluxes. The long-term, steady flux of a solute due to diffusion (J_d) is given by Eq. 4. Typical values are assumed for a clay liner: $D^* = 2 \times 10^{-10}$ m^2/s, $\theta = 0.5$, concentration of solute in leachate = c, concentration of solute in soil beneath the liner is zero, and thickness of liner = 1 meter. For these conditions:

$$J_d = \left(1 \times 10^{-10}\ m/s\right) c \qquad (9)$$

For the same liner, the advective flux for unit hydraulic gradient is:

$$J_a = k\,c \qquad (10)$$

The total flux (J) is

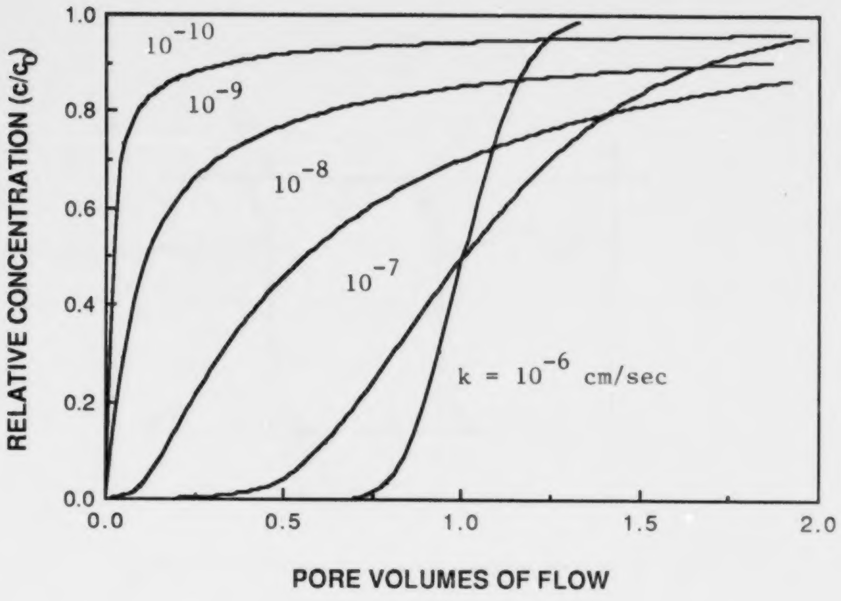


Figure 6. Breakthrough curves for a 3-ft-thick clay liner.

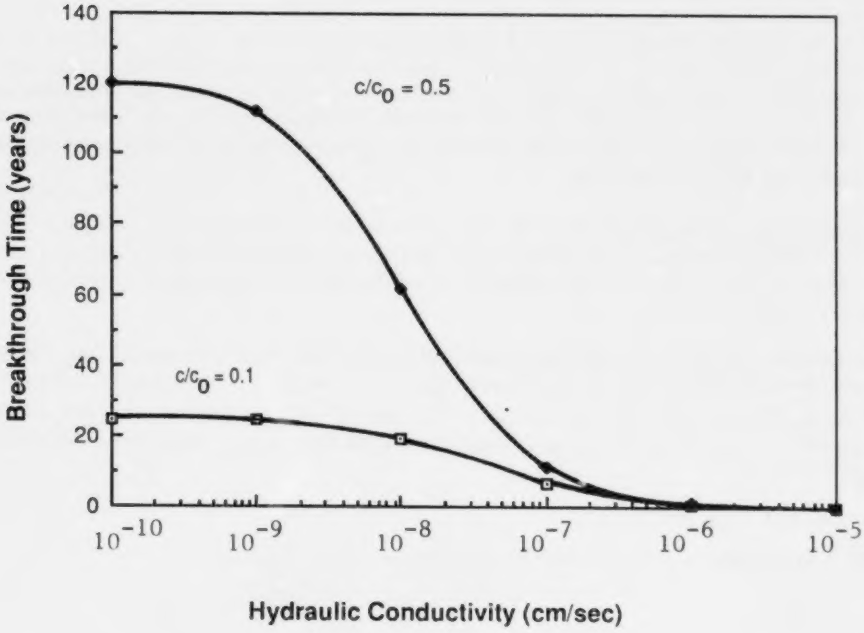


Figure 7. Breakthrough time versus hydraulic conductivity for a 3-ft-thick clay liner.

$$J = J_a + J_d = \left(1 \times 10^{-10}\ \text{m/s} + k\right) c \tag{11}$$

or:

$$\frac{J}{c} = 1 \times 10^{-10}\ \text{m/s} + k \tag{12}$$

The mass flux per unit concentration (J/c) is plotted as a function of the hydraulic conductivity of the liner in Fig. 8. For hydraulic conductivities less than 10^{-8} to 10^{-9} cm/s, the mass flux is essentially constant and is controlled by J_d. The percent of total flux caused by diffusion is:

$$\frac{J_d}{J} \times 100\% = \frac{1 \times 10^{-10}\ \text{m/s}}{1 \times 10^{-10}\ \text{m/s} + k} \tag{13}$$

The percentage of flux caused by diffusion is plotted as a function of the hydraulic conductivity of the liner in Fig. 9. For hydraulic conductivities less than 10^{-7} cm/s, advection is responsible for nearly all the mass flux. At a hydraulic conductivity of 10^{-8} cm/s, advection and diffusion each account for half of the mass flux. At hydraulic conductivities less than 10^{-9} cm/s, diffusion is the source for nearly all the mass flux.

CONCLUSIONS

Solutes are transported through compacted clay soil both by advection and diffusion. Experiments have shown that the effective diffusion coefficient for anions diffusing through compacted clay soils is about 2×10^{-10} m^2/s. Cations tend to diffuse more slowly due to ion exchange and other reactions. The method of compaction and molding water content have little influence upon the effective diffusion coefficient of compacted clay soil. However, subtle variations in geochemical factors, e.g., concentration of a solute in leachate or cation exchange capacity of the soil, can cause significant changes in the rate of diffusive transport through clay soils.

For typical clay liner thicknesses (3 ft or approximately 1 m) and hydraulic gradients (slightly greater than 1), advection dominates the flow of solutes through compacted clay liners having hydraulic conductivities of 1×10^{-7} cm/s or greater. Diffusion becomes the dominant mechanism of transport at hydraulic conductivities on the order of 10^{-8} to 10^{-9} cm/s or less. Solutes can travel through a 3-ft-thick clay liner of zero hydraulic conductivity purely by diffusion in periods of 10 - 30 years or less. To ignore molecular diffusion in clay liners having hydraulic conductivities significantly less than 10^{-7} cm/s is to ignore an important, if not dominant, mechanism of solute transport.

REFERENCES

1. Daniel, D. E. Earthen Liners for Land Disposal Facilities. In: Geotechnical Practice for Waste Disposal '87. American Society of Civil Engineers, New York, 1987. pp. 21-39.

2. Freeze, R. A., and Cherry, J. A. Groundwater. Prentice-Hall, Englewood Cliffs, New Jersey, 1979. 604 p.

3. Quigley, R. M., Yanful, E. K., and Fernandez, F. Ion Transfer by Diffusion through Clayey Barriers. In: Geotechnical Practice for Waste Disposal '87. American Society of Civil Engineers, New York, 1987. pp. 137-158.

4. Goodall, D. E., and Quigley, R. M., Pollutant Migration from Two Sanitary Landfill Sites Near Sarnia, Ontario. Canadian Geotechnical Journal, Vol. 14, 1977. pp. 223-236.

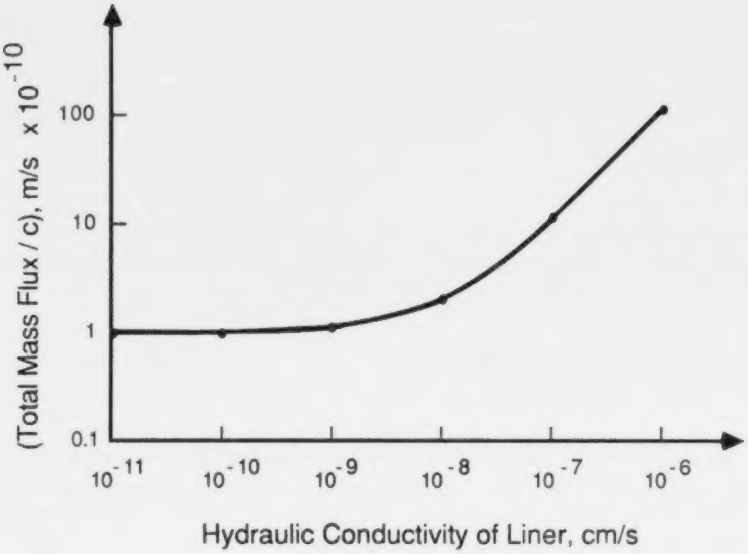


Figure 8. Mass flux versus hydraulic conductivity for a 1-m-thick liner having an effective diffusion coefficient of 2×10^{-10} m^2/s.

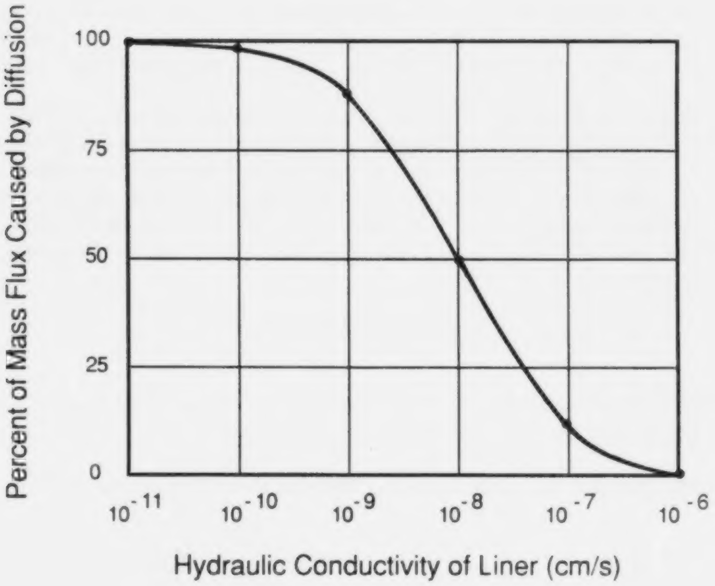


Figure 9. Percent of mass flux caused by diffusion versus hydraulic conductivity for a 1-m-thick liner.

5. Gillham, R. W., Robin, M. J. L., Dytynyshyn, D. J., and Johnston, H. M. Diffusion of Nonreactive and Reactive Solutes through Fine-Grained Barrier Materials. Canadian Geotechnical Journal, Vol. 21, 1984. pp. 541-550.

6. Quigley, R. M., and Rowe, R. K. Leachate Migration through Clay below a Domestic Waste Landfill, Sarnia, Ontario, Canada. ASTM STP 933, 1986. pp. 93-103.

7. Rowe, R. K. Pollutant Transport through Barriers. In: Geotechnical Practice for Waste Disposal '87. American Society of Civil Engineers, New York, 1987. pp. 159-181.

8. Horton, R., Thompson, M. L., and McBride, J. F. Estimating Transit Times of Noninteracting Pollutants through Compacted Soil Materials. In: Proceedings of the Eleventh Annual Research Symposium on Land Disposal of Hazardous Waste, U.S. EPA, Cincinnati, Ohio, EPA/600/9-85/013, April, 1985. pp. 275-282.

9. Bowders, J. J., Daniel, D. E., Broderick, G. P., and Liljestrand, H. M. Methods for Testing the Compatibility of Clay Liners with Landfill Leachate. In: Hazardous and Industrial Solid Waste Testing, Fourth Symposium, STP 886, American Society for Testing and Materials, Philadelphia, Pennsylvania, 1985. pp. 223-250.

10. Olsen, S. R., Kemper, W. D., and Van Schaik, J. C.. Self-Diffusion Coefficients of Phosphorous in Soil Measured by Transient and Steady-State Methods. Proc. Soil Sci. Soc. America, 29:154, 1965.

11. Crank, J. The Mathematics of Diffusion, 2nd Edition. Clarendon Press, Oxford, England, 1974, 414 p.

12. Shackelford, C. D. Diffusion of Inorganic Chemical Wastes in Compacted Clay. Ph.D. Dissertation, The University of Texas, Austin, Texas, 1987, 449 p.

13. Rhoades, J. D. Soluble Salts. In: A. L. Page, R. H. Miller, and D. R. Keeney (eds.), Methods of Soil Analysis, Part 2, Second Edition. American Society of Agronomy, Madison, Wisconsin, 1982. pp. 167-179.

14. U.S. Environmental Protection Agency. Batch-Type Adsorption Procedures for Estimating Soil Attenuation of Chemicals. EPA/530-SW-006. Draft Technical Resource Document for Public Comment, Cincinnati, Ohio. (NTIS PB87-146-155).

15. Ogata, A. Theory of Dispersion in Granular Medium. U.S. Geological Survey Professional Paper 411-1, 1970.

U. S. EPA RESEARCH IN SOLIDIFICATION/STABILIZATION OF WASTE MATERIAL

by: Carlton C. Wiles and Hinton K. Howard
U. S. Environmental Protection Agency
Cincinnati, Ohio 45268

ABSTRACT

Solidification and stabilization (S/S) technologies for the management of hazardous wastes have a high level of importance, particularly with regard to treating contaminated soils at Superfund sites and with regard to treating residuals from other treatment technologies. This paper presents a summary of recently completed, ongoing, and planned research by the U.S. EPA to provide the best possible information regarding the utilization of solidification/stabilization processes. Areas include studies of existing protocols and processes. studies of basic chemical and physical mechanisms, and applicability to a variety of wastes.

INTRODUCTION

The Resource Conservation and Recovery Act (RCRA) and the more recent Hazardous and Solid Waste Amendments have provisions aimed at reducing the use of land disposal for the management of hazardous wastes. It is clear that the most satisfactory solutions to hazardous waste problems are those which either destroy or detoxify the wastes. However, for the near future, there exist wastes which can not be destroyed or detoxified, but only reduced in volume or contained. These wastes and the residues from their treatment will continue to be managed by land disposal until new technologies for their total destruction emerge. Solidification and stabilization will continue to have a high level of importance for these wastes and in the treatment of contaminated soils at Superfund sites.

The solidification/stabilization technologies are applicable to the treatment of selected banned waste prior to landfilling. They are also applicable to the treatment of residues from other treatment technologies. The broad objectives are either to contain pollutants and prevent them from entering the environment, or to transform the toxic materials into nontoxic forms. The containment objective is addressed with processes which may produce a solid, decrease the surface area across which contaminants can be transported, limit the mobility of contaminants exposed to leaching or improve the handling characteristics of the waste. The detoxifying objective is addressed with processes which involve a chemical change and the formation of new compounds.

OBJECTIVE OF SOLIDIFICATION/STABILIZATION RESEARCH

The objective of research on solidification/ stabilization is to provide the technology which allows the complete transformation of toxic wastes to non-toxic forms. This objective implies chemical transformation and formation of new compounds which does not routinely occur with most of today's available state-of-the-art S/S technologies. Some chemical concepts have, however, been proposed which could improve the potential for meeting the ideal objective. These concepts include passivation or armoring reactions, elemental substitution or diadochy, chemisorption and production of new insoluble compounds. Passivation is the chemical coating of a substance with a rind that prevents further chemical attack. Diadochy is a process that removes elements from the environment by substitution during precipitation of commonly occurring compounds. Different ions have the ability to occupy the same lattice position in a crystal structure. Therefore, elements with similar sizes and charges can substitute for one another in common crystal lattices. Toxic elements can be substituted in stable crystal systems that can prevent release of the element to the environment.

The most important technical needs involve developing a scientific understanding of the S/S processes. In order for S/S technology to be effective in managing hazardous waste, it is critical that process candidates be properly selected, formulated, and used. There are several factors important in the selection and subsequent performance of candidate processes. These include waste chemical and physical characteristics; binder physical and chemical characteristics; interactions of binder/waste, and impurities in the matrix; product placement regime and others. Knowledge of these factors and the interactions which can be expected among the various candidate binders and waste types is critical to the successful use of and evaluation of S/S for managing hazardous waste. This knowledge is also critical to the successful formulation and implementation of a regulatory strategy and technical guidance for the technology.

Knowledge of the S/S binders and how they are expected to react under different uses and with different wastes can provide valuable insight into processing requirements, waste pretreatment requirements, waste-binder interactions, and expected product performance. Governmental and other research efforts have concentrated on cement-lime/fly ash-pozzolanic processes. Additional efforts are required in this area. However, more basic research needs to be conducted on other binders.

Although S/S technologies have been used for more than 20 years, there exists little information on long-term physical durability and chemical stability of the S/S mass when placed in the ground. In addition, past S/S processors have not been driven by regulatory factors (i.e., waste banning, liquids in landfills, etc.) which force current users to meet more stringent performance requirements. Therefore, measuring the performance of previous S/S waste applied to the land, although useful, may not be a complete source of data, because future S/S processes will be required to meet much more stringent performance criteria. Studies are required to determine the long-term physical-chemical stability of S/S residues when placed on the land. Studies are also required to determine how and under what conditions S/S residues should be placed in order to ensure environmental protection over the long term.

Prediction and measurement of the performance of S/S processes and products is an area of concern, and needs to be more fully investigated. Current efforts have begun to evaluate effectiveness of several protocols to characterize S/S products. This work needs to be extended to provide effective measurement techniques. More important, however, research needs to correlate results of such tests with prediction of performance in the field.

Generally, S/S technology is recognized effective for inorganic waste, while organic wastes have the potential to cause problems. More information is required on how much organic waste may be included in inorganic waste without requiring pretreatment prior to S/S. The long term effects of organics on S/S performance are important, however, little research has been performed. This is particularly important for the remediation of high volume, low level contaminated soils and debris.

SOLIDIFICATION/STABILIZATION RESEARCH PROGRAM

Currently, the U.S. EPA is evaluating S/S as a best demonstrated available technology for treating hazardous waste. Also involved are evaluations for treating contaminated soil and debris, and research to develop a more comprehensive scientific understanding of the technology.

The current U.S. EPA research (Table 1) has emphasized investigating interferences to S/S, wastebinder interaction, waste disposition sites, and methods for predicting performance of S/S products.

Research on interfering agents will provide data on the effects interfering inorganics (Pb, Cd, Zn, sulfates, etc.) and organics (oil, grease, HCB, TCE, phenol) may have on commonly used pozzolanic binder systems. The information will be useful in evaluating applications for delisting hazardous waste and for permits to treat hazardous wastes with S/S, particularly for those waste streams contaminated with organics. This information and that from research on factors critical to S/S will also aid decisions on potential waste pretreatment techniques for enhancing S/S performance. Data from physical and chemical tests is being analyzed to determine if a correlation exists between physical properties of the solidified waste form and its ability to resist stresses when exposed to leaching situations.

An effort with Environment Canada emphasizing the evaluation of several leaching tests will determine the extent of toxic constituent within the binding. Protocols for examining physical properties are also being evaluated. This research includes actual waste and synthetic sludges solidified by vendors. Information on the performance of several different solidified products will be compared. This research will provide important data to compare current U.S. EPA regulatory leaching procedures with others being tested.

Electron scanning and x-ray defraction microscopy techniques along with solvent extractions are being used to investigate waste/binder interactions. The objective is to better understand S/S processes by identifying binder reaction phases and where the waste components concentrate their form and are bonded. Concurrent with this research, specimens of solidified waste from other research projects are being examined in efforts to correlate results of physical and chemical tests with performance of S/S products. Results from these specific studies have indicated that physical entrapment of inorganic metals is a predominant containment mechanism. However, some results are also indicating formation of altered or new crystal structures in some phases which appear to be chemically bonding some organics. Indications are that this type research could provide information useful in preparing binder formulations better able to treat a specific waste.

The physical and chemical characteristics of the waste affect the performance, as do the climatic (temperature and humidity) conditions at the time of placement and curing. The research on critical characteristics is being expanded to develop information on what quality assurance/control procedures are needed to better assure performance of S/S when applied in the field. This information is especially important for the remediation of contaminated soils with varying characteristics and field treatment projects requiring more than one season.

Because of the nature of many solidification processes, uncontrolled air emissions are a potential problem to workers and the environment. Investigations are being conducted to determine the magnitude of these air emissions. Processes being evaluated are Portland cement - fly ash and lime kiln dust - fly ash mixtures. As expected, mixing causes the greatest air emissions. Some additives such as lime result in exothermic reactions which increases the release of volatile compounds. Capture and treatment of these emissions may be required to protect worker health and the environment, particularly in cases where the waste or contaminated soils contain volatile compounds.

A variety of leaching tests are used to predict how well the solidified waste form will prevent the release of contaminants over time. To assure the proper use of these procedures, an effort (not shown on Table 1) is being initiated to compile and evaluate available information on the procedures to determine the correct use, how well each performs its intended function, and which ones are best suited to better predict long term performance. This is especially important for the proper design of S/S processes for remediating contaminated soils and debris.

TABLE 1. Current U.S. EPA Solidification/Stabilization Research Projects

Project Title	Objective	Status
Evaluation of Factors Affecting Solidification/ Stabilization of Toxic Waste	Determine effects of interfering agents on performance of S/S	Data interpretation ongoing
Investigation of Test Methods for Solidified - Waste Characterization - A Cooperative Program	Develop and evaluate methods for testing performance of solidification processes	Data interpretation ongoing
Study of Morphology and Microchemistry of Solidified/ Stabilized Waste	Investigate bonding mechanisms	Research is continuing
Morphological Examination of S/S Samples from Canadian - US and other studies	Morphological examination of solidified waste specimens; correlate results with physical/ chemical test of actual samples	Ongoing
Critical Characteristics of Hazardous Waste Solidification/ Stabilization	Identify physical and chemical characteristics of waste and binders affecting S/S	Being expanded to provide QA/QC information
Air Emissions from Waste Stabilization	Determine air emissions from S/S processes	Ongoing
Evaluation of S/S for Treating Ash Residues	Evaluate S/S of residues from combusting municipal solid waste	Ongoing

Ashes from the combustion of municipal waste may contain unacceptable levels of heavy metals, particularly lead and cadmium. Solidification/Stabilization technology is being evaluated as an acceptable technique to control leachate from the ashes if required.

EVALUATION OF S/S AS AN AVAILABLE TREATMENT TECHNOLOGY

The Hazardous and Solid Waste Amendments (HSWA), which amended the Resource Conservation and Recovery Act (RCRA) provide detailed procedures dictating how hazardous waste is defined, controlled, and managed. Wastes classified as hazardous under RCRA are often referred to as RCRA hazardous waste. Key provisions of HSWA are the ones which ban the land disposal of hazardous waste unless it is proven to be more protective of the environment and human health than other alternatives. The legislation requires that all hazardous waste be treated by the best demonstrated available technology (BDAT) instead of and prior to land disposal. The U.S. EPA is required to determine and specify levels to which BDAT technologies can treat RCRA waste. Solidification/Stabilization is one of several BDAT technologies being evaluated. In this program selected hazardous wastes are solidified/stabilized by Portland cement, cement kiln dust, and lime/fly ash mixtures. Various ratios of waste to binder for each binder system are then evaluated by the Unconfined Compressive Strength Test (UCS) after a cure time of 7, 14, 21, and 28 days. Cured samples are then subjected to the USEPA's Toxicity Characteristic Leaching Procedure (TCLP) extraction test. Leachate from the TCLP is analyzed for the pollutants of concern (Table 2), to determine how effective S/S can be for treating selected hazardous waste. Results will be used to treat hazardous waste in the U.S.

The remediation of contaminated soils, hazardous waste uncontrolled dump sites, etc., is controlled under legislation referred to as the Superfund Amendments and Reauthorization Act (SARA) which amended the Comprehensive Environmental Reclamation Compensation Liability Act (CERCLA). Under SARA provisions, permanent treatment of the contaminated soil and debris is being emphasized rather than the use of nontreatment containment systems such as covers, grout walls, and similar methods. Because of this, a program similar to the RCRA BDAT evaluations is being conducted for SARA remediation technologies including S/S. Mixtures of soils contaminated with selected chemicals (Table 3) are solidified/stabilized and tested to evaluate performance of S/S technology for treating contaminated soils. The test soil being used is a mixture of clay, sand, silt, topsoil and aggregate.

In conjunction with other evaluation programs, laboratory facilities and procedures have been established to test samples of solidified waste extracted from bench and pilot treatability studies and field operations. These facilities also assist in determining if a particular contaminated soil or waste is capable of being effectively solidified/stabilized by using a full range of leaching and physical tests. Data from this program will help investigators to extrapolate laboratory test results to better predict expected long term field performance.

SUPERFUND INNOVATIVE TECHNOLOGY EVALUATIONS (SITE)

The U.S. EPA SITE program provides for demonstration and evaluation of innovative technologies to remediate Superfund sites. Currently, six S/S processes are being evaluated (Table 4). Results will provide information on how well S/S can be expected to permanently treat contaminated soils. The evaluations will also help make better extrapolation of laboratory tests results to field conditions.

PROCESS SELECTION CONSIDERATIONS

Factors important in the selection, design, implementation, and performance of processes and products are: waste characteristics (chemical and physical), processing requirements, S/S product management objective, regulatory requirements, and economics. These and other site-specific factors (i.e., location, condition, climate, hydrology, etc.) must be carefully considered to ensure acceptable performance.

The chemical effects of some compounds can reduce the strength of the binder/waste mix, while some compounds can accelerate or retard the S/S curing rate. Temperature and humidity can also retard or accelerate curing. Size and shape of the waste particles can affect the viscosity of the mix. Overmixing or undermixing can affect the product's strength. Waste characteristics are among the most important factors affecting S/S and inorganics usually can be more easily solidified/ stabilized than can organics.

It is important to assess what process type and specific process requirements are required before selecting an S/S technology. For example, a wastebinder can be controlled and mixed more easily in a drum or in a plant process than in the in-situ solidification of a pit, pond, or lagoon.

How the solidified waste will be managed is important in selecting the best process. Will it be disposed of in a landfill, or stored, or transported? Will it be placed in a plastic or metal drum below or above the water table? Stored in a warehouse or underground mine?

Regulations in the United States will be critical to the success of S/S. Processes can be altered to meet different performance criteria, which will become increasingly stringent, as regulations become more stringent. S/S will be competing with other treatment technologies to meet these regulatory criteria.

Costs will depend on site-specific conditions. Important are the waste's characteristics, transportation, type of process, and other special factors. What is the physical form and chemical make-up of the waste? Is pretreatment needed? Is transportation of raw materials and/or finished S/S products required? Which S/S process is needed? What special health and safety requirements are needed? What is the quality assurance/quality

TABLE 2. Examples of U.S. RCRA Hazardous Wastes for Which S/S is Being Evaluated as a Treatment Technology

Waste Code	Description of Waste	Pollutant of Concern
K048-52	Dissolved air flotation (DAF) float from the petroleum refining industry	Hexavalent chromium, lead
K061	Emission control dust/sludge from the primary production of steel in electric furnaces	Hexavalent chromium, lead, cadmium
K046	Wastewater treatment sludges from manufacturing, formulation, and loading of lead-based initiating compounds	Lead

TABLE 3. Contaminants Added to Test Soil Being Used to Evaluate Effectiveness of Solidification for Treating Soils

Metals	Volatiles	Semi-Volatiles
Lead	Acetone	Benzo (a) pyrene
Zinc	Ethylbenzene 1,2 Dichloroethane	Pentachlorophenol
Cadmium	Xylene	Naphthalene
Copper	Tetrachloroethylene	
Nickel	Chlorobenzene	
Chromium		

control cost involved? What regulatory criteria must be met? Each of these factors must be considered. As regulatory criteria become more demanding, the costs of acceptable solidification processes may increase.

STUDIES NEEDED FOR S/S AS A TREATMENT TECHNOLOGY

For S/S technology to be effective in managing hazardous waste, proposed processes must be properly selected, formulated, and used. Improved

TABLE 4. Solidification/Stabilization Processes Being Evaluated in the U.S. EPA SITE Program

Process Developer	Description
Chemfix Technologies, Inc.	Uses soluble silicate reagents and silicate-setting agents
Soliditech, Inc.	Uses pozzolanic agents, water and liquid reagents including URRICHEM. Claims to treat organics and inorganics
Waste Chem Corporation	Volume reduction and solidification using asphalt binder and extrusions. Claims to treat organics and inorganic metals
Battelle Pacific NW	In Situ vitrification; thermal treatment to pyrolyze organics and immobilize inorganics in glass-like mass
Hazcon, Inc.	Uses Portland cement, fly ash, kiln dust and proprietary chemicals to treat organics and inorganics
International Waste Technologies	Uses silicate-colloid or inorganic polymers as medium; promotes adsorption of organics; claims chemical bonding of organics; treats inorganics

knowledge of process selection considerations and the interactions among the various candidate binders and waste types is critical to the successful use as an acceptable treatment technology.

Studies are needed:

- ° to determine the long-term physical-chemical stability of S/S products when placed on the land;
- ° to determine how and under what conditions S/S

products should be placed on the land to ensure long term environmental protection;

- to more accurately predict and measure the performance of S/S processes and products;
- to provide a correlation between regulatory criteria and real world situations;
- to evaluate the effectiveness of protocols (e.g., TCLP, other leaching tests, UCS, etc.) to characterize S/S products, provide effective measurement techniques, and correlate results of such tests with performance in the field;
- to determine the effectiveness of processes and equipment to effectively solidify/stabilize contaminated soil and/or lagoons; the effectiveness of mixing methods; and the resulting solidified/stabilized soil performance at varying soil depths;
- to determine the amounts of organic compounds that can be included in inorganic waste streams without requiring pretreatment before S/S;
- to determine how effectively S/S processes treat residuals compared to other alternative treatments.

SUMMARY

Solidification/Stabilization is being evaluated by the U.S. EPA as a best demonstrated available technology for treating hazardous waste and contaminated soils and debris. Future use of the technology in the United States will depend on how well it performs compared to other available treatment processes. Current research being conducted will provide some answers regarding performance, however, additional studies are required for a better scientific understanding of S/S. Whether or not S/S becomes an important technology for treating hazardous waste and contaminated soils in the U.S. ultimately depends upon regulatory requirements and the capability of the technology to meet these requirements. As performance criteria become more severe, S/S developers may need to improve their processes. The opportunity is very good. In the case of RCRA waste, S/S may be the only acceptable method to treat selected inorganic waste and hazardous residues from incinerators and other treatment processes. In the case of contaminated soils and debris, S/S offers a relatively inexpensive method for treating large areas in-situ. However, the capability of the technology to perform satisfactorily over long periods of time has yet to be determined.

SITE DEMONSTRATION OF HAZCON SOLIDIFICATION/STABILIZATION PROCESS

by: Paul R. de Percin
Hazardous Waste Engineering Research Laboratory
U.S. Environmental Protection Agency
Cincinnati, Ohio 45268

Stephen Sawyer
Enviresponse Inc.
Edison, New Jersey 08837

ABSTRACT

Concern has been increasing in the United States over the use of landfills for the containment of hazardous wastes. In response to this concern, the U.S. Environmental Protection Agency (USEPA) has established a formal program to accelerate the development and demonstration of new and innovative waste treatment technologies. This program is called the Superfund Innova-Technology Evaluation Program or SITE.

One of the new innovative technologies demonstrated under the SITE program was the HAZCON solidification/stabilization process. This process blends contaminated soil or sludge with cement, pozzolans, and a proprietary ingredient called Chloranan which neutralizes the inhibiting effects of organics. A concrete-like mass is the result.

The demonstration of the HAZCON process took place in October 1987 at the Douglassville Superfund site along the Schuylkill River near Reading, Pennsylvania. This rural site is a 50 acre plot that is contaminated with high levels of oil and grease and low levels of PCBs, and volatile and semivolatile organics from the operations of an oil reprocessing plant. Soil samples from six different plant areas were processed to test the capability of the HAZCON process on a diverse set of site wastes.

The primary criteria for evaluating the HAZCON process are: 1) reduced contaminant mobility, and 2) integrity of the solidified soil mass. To obtain the evaluation data, samples were taken from the untreated soil, the blended slurry (after 7 days of curing), and from the solidified blocks (after 28 days of curing). The samples were analyzed for soil characteristics, leachability, permeability, unconfined compressive strength, microstructural characteristics, and levels of contaminants.

BACKGROUND

In response to the Superfund Amendments and Reauthorization Act of 1986 (SARA), the U.S. Environmental Protection Agency's Offices of Research and Development (ORD) and Solid Waste and Emergency Response (OSWER) have established a formal program to accelerate the development, demonstration, and use of new or innovative technologies as alternatives to current containment systems for hazardous wastes. The new program is called the Superfund Innovative Technology Evaluation program or SITE.

The major objective of a Demonstration Test Program is to develop reliable cost and performance information. One candidate technology, which was demonstrated in October 1987 at the Douglassville, Pennsylvania Superfund Site, is the HAZCON proprietary solidification process. The process involves the intimate mixing of hazardous waste material and cement with a patented nontoxic chemical called Chloranan. Chloranan, according to HAZCON, neutralizes the inhibiting effects that organic contaminant materials have on cement reactions. For this treatment, the wastes are immobilized and bound into a hardened, leach-resistant concrete-like mass.

The Douglassville, Pennsylvania Superfund Site, No. 102 on the National Priority List, was selected as the location for the Demonstration Test. This is a 50 acre rural site that was an oil recovery facility. The site includes: two large lagoons once filled with oily sludge, an oily filter cake disposal area, an oil drum storage area, an area where generated sludge was landfarmed into the soil and the plant processing area. An estimated 250,000 cubic yards of soil may be contaminated.

PROGRAM OBJECTIVES

The major objectives of the SITE program are to determine the following:

1. The ability of the HAZCON process to immobilize the contaminants at the Douglassville, Pennsylvania Superfund Site
2. The potential integrity of the solidified soils, and
3. The field reliability of the equipment used to process the different wastes at the site.

DEMONSTRATION PROGRAM

Contaminated soils at the Douglassville, Pennsylvania Superfund Site were processed by HAZCON using a truck mounted system. This system blended the contaminated soils with portland cement, water and Chloranan (a proprietary chemical) to create a solidified material.

Six different contaminated soils at the Douglassville, Pennsylvania site were processed by HAZCON from the following locations; 1) lagoon north (LAN), 2) lagoon south (LAS), 3) filter cake storage area (FSA), 4) drum storage area (DSA), 5) plant facility area (PFA), and 6) landfarm area (LFA). The intent was to process enough soil to yield a treated volume of 5 cubic yards from each of 5 areas. An extended duration run for the sixth area was to determine the reliability of the operating equipment. Approximately 25 cubic yards of LAS contaminated soil was to be treated. The actual runs used less soil, but resulted in approximately 5 and 25 cubic yards of treated soil.

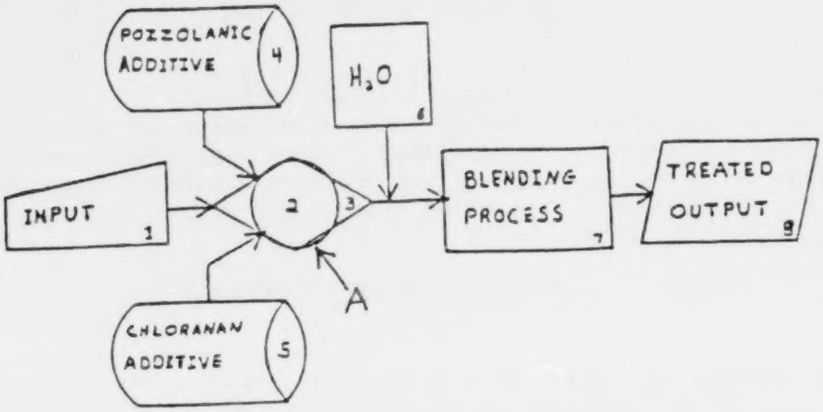
The contaminated soil was excavated and screened to remove material greater than 3 inches. It was then fed into the HAZCON Mobile Field Blending Unit (MFU - the truck mounted system) along with #1 portland cement, water and Chloranan. Cement was used on an approximately 1:1 basis with soil and the soil to Chloranan ratio was 10:1. The four feed components were blended in a mixing screw and fed to 5 one-cubic yard wooden molds for the short tests and 3 one-cubic-yard plus two 12 cubic yard pits for the LAS. During the processing of the three soils lowest in organics (DSA, LFA and PFA), toluene was injected into the soil to attain a concentration of 100 ppm. It was felt that this would provide leachate concentrations of sufficient magnitude to be above the analytical detection limits.

While the contaminated soil was processed and cured, the excavation holes were enlarged, lined with an impervious plastic liner, and partially filled with clean soil. After the one cubic yard blocks cured sufficiently to be moved (48-96 hours), they were removed from the molds and placed into the pits. The blocks were then covered with additional clean soil. After 28 days, the blocks were sampled. It is planned that 6 and 12 months after burial the blocks be sampled again to develop long-term test results.

PROCESS DESCRIPTION

HAZCON Engineering, Inc.'s Mobile Field Blending Unit (MFU) operates as a continuous processing unit. The Mobile Field Blending Unit Flow Diagram followed by a description of each operation (number to number) is shown in Figure 1. Operating capacities, though governed by predetermined mix ratios set in the laboratory, are variable by up to 12 cubic yards of processed raw waste per operating hour. The MFU has no external utility requirements other than a standard water hook up and the attachment of a "quick connect" line from a bulk cement carrier. The equipment obtains its driving power from the diesel engine of the MFU vehicle.

Equipment calibration was performed each time a new waste feed material entered the MFU. Calibration involves the determination of the waste and cement feed by weight, for a set of given feed screw settings. Feed rates were confirmed during the run by using a bag counter for cement, a flow totalizer for water and tank level change for Chloranan.



1. Waste material is introduced to the system through the use of pumps, dredges, or earth moving equipment, whichever may be the most efficient or practical.

2. The waste is moved through the process in a controlled flow, allowing for precise measurement of the material.

3. Based upon these measurements, blending ratios, which are predetermined in the laboratory, are set on a time weighted basis for both the Chloranan and pozzonalic material, such as portland cement. The Chloranan is a proprietary additive that reduces the inhibiting effects of organics in the crystallization of cement.

4. The pozzolanic ingredient is stored in a hopper and then metered into the mix. Typical ratios, on a weight basis, range from 1 part waste: 1 part pozzolan, to 3 parts waste: 1 part pozzolan. For the test at the Douglassville site, a ratio of 1:1 was used.

5. Chloranan is stored in a holding tank, then pumped into the mixing chamber. Through precise control of the flow rate, ratios of waste to Chloranan can be accurately metered from a 10:1 to a 50:1 blend.

6. After initial combination of the primary ingredients, water may be added as necessary to achieve the most desirable slump on the mix.

7. All additives are fed via pump or auger through a mixing chamber to achieve a homogenous blend.

8. The resultant mass was extruded into either temporary or permanent molds.

Note: The injection point (A) for toluene addition, which was added to the three least contaminated soils, was at the inlet of the blending auger.

Figure 1. Mobile Field Blending Unit Flow Diagram

EQUIPMENT SPECIFICATIONS

The mobile field blending unit is shown in Figure 2. A separate bulk cement carrier was provided for feeding to the cement bin on the equipment trailer carrying the MFU. In addition, a water supply truck was provided for process water and for feeding high pressure equipment decontamination water. Also, Chloranan was supplied from a tank on the auxiliary trailer provided by HAZCON.

SAMPLING AND ANALYSIS PROGRAM

Soil samples were taken before treatment, as a slurry exiting the MFU for analysis after 7 days and as cores from the buried blocks after 28 days of curing. For the 5 cubic yard blocks, two untreated soil composite samples were taken along with 3 sets of slurry and solidified cores. For the extended run at LAS, additional samples were taken for analysis.

The specific analyses performed on soil, slurry and core samples included measuring physical properties, those being:

- bulk density
- moisture content
- permeability (liquid)
- unconfined compressive strength of the solidified cores
- weathering tests for the 28-day core tests (wet/dry, freeze/thaw)

Chemical analyses were performed to identify the volatile organics, base neutral acid extractables (BNAs or semivolatiles), polychlorinated biphenyls (PCBs) and metal contaminants in the processed soil. In addition, three different leaching tests were run:

- toxicity characteristic leaching procedure (TCLP) - standard leaching procedure used for measuring leachability of the organic and metal contaminants.
- ANS 16.1 - simulates leaching from the intact solidified core with rapidly flowing groundwater (ANS - American Nuclear Society).
- MCC-IP - simulates leaching from the intact solidified core in relatively stagnant groundwater regimes (MCC - Materials Characterization Center, Richland, Washington).

These latter two tests were drawn from the nuclear industry and modified to hazardous waste analyses. Unlike the USEPA procedure that grinds the solidified sample to a fine grain size, the ANS and MCC procedures leach the intact sample.

Finally, microstructural studies were performed on the untreated soil and solidified cores. These analyses included:

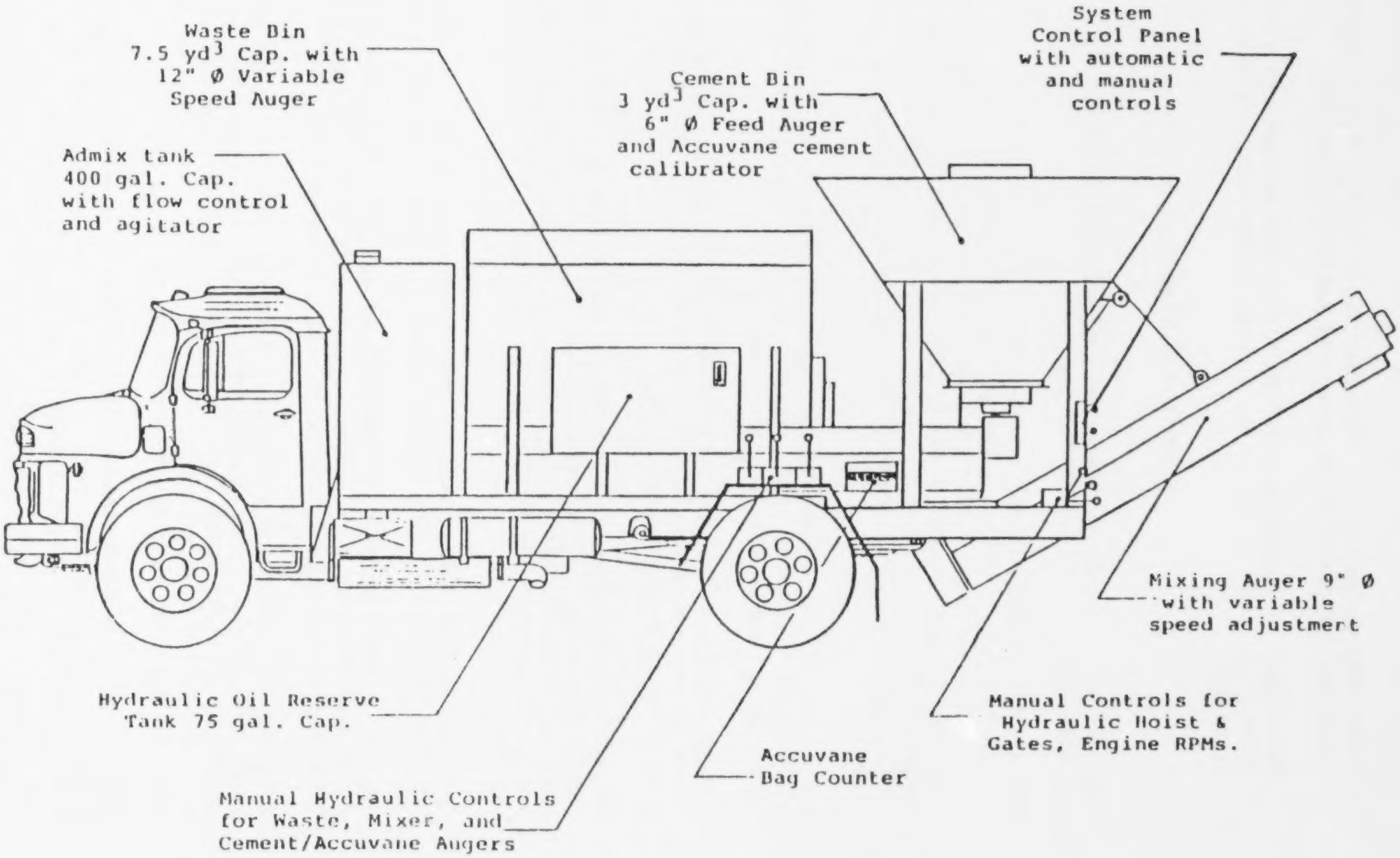

Waste Bin
7.5 yd3 Cap. with
12" Ø Variable
Speed Auger
Admix tank
400 gal. Cap.
with flow control
and agitator
Cement Bin
3 yd3 Cap. with
6" Ø Feed Auger
and Accuvane cement
calibrator
System
Control Panel
with automatic
and manual
controls
Mixing Auger 9" Ø
with variable
speed adjustmert
Hydraulic Oil Reserve
Tank 75 gal. Cap.
Manual Controls for
Hydraulic Hoist &
Gates, Engine RPMs.
Accuvane
Bag Counter
Manual Hydraulic Controls
for Waste, Mixer, and
Cement/Accuvane Augers

Figure 2 Equipment Layout Diagram

° X-ray diffractometry - characterizes porosity, hydration products, fractures and presence of unreacted soil/waste material

° Microscopy - scanning electron microscope and optical microscope - identifies level of porosity, crystal appearance, agglomerates, and fractures.

RESULTS - GENERAL

Not all of the analyses have been completed at this time, however, the results obtained-to-date are as follows:

1. The six test areas offered a wide diversity of waste. The oil and grease ranged from 1% by weight at the DSA to 25% at FSA. Polychlorinated biphenyls (PCBs) were detected up to 80 ppm by weight with the maximum concentration at LAS. Lead contamination concentrations ranged up to 2.5% by weight. Volatiles and base neutral acid extractables (BNAs - semivolatiles) organics reached levels of about 100 ppm in some areas.

2. The volume of the solidified soil was approximately double that of the undisturbed feedstock. Approximately an equal amounts of soil and cement were used in the demonstration.

3. Permeabilities of the treated soil were very low, in the range 10-8 to 10 -9 cm/sec. A value of 10-7 or less is generally considered an indication of an impermeable solid.

4. The unconfined compressive strengths (UCS) of the solidified soils ranged from about 200 psi for FSA to 1500 psi for PFA and the values were inversely proportional to the oil and grease concentration. These values are quite satisfactory from a load bearing point of view, i.e., equipment traffic.

5. Only the TCLP leaching tests, of the three leaching tests performed, have been completed. The results shown in Table 1 are discussed below:

   Metals - the leachates for the solidified soils showed metal levels at or near the detection limits. The results were a factor of 500 to 1000 less than in the leachates for the untreated soils.

   Volatiles - the primary compounds detected were trichloroethene, tetrachloroethene, toluene and xylenes. Only the leachates for the untreated soil and 7-day cores were analyzed. The levels of contaminants were approximately the same in both the treated and untreated soils, each at levels of hundreds of micrograms per liter.

   BNAs - the compounds detected in the leachates were phthalates and phenols. The phthalates were reduced to near their detection limits of 10 ug/l in both the treated and untreated soil leachates. The total

TABLE 1. RESULTS OF TCLP LEACHING TEST

Plant	Soil Concentrations, ppm			Leachate Untreated Soil, mg/l			Leachate Treat Soil - 7 days, mg/l		
Area	Lead*	VOC[+]	BNA°	Lead	VOC	BNA	Lead	VOC	BNA
DSA	3,230	ND[¶]	18	1.5	0.7§	ND	ND	0.4	0.06
LAN	9,250	2	20	33.	0.03	1.1	0.01	0.01	1.3
FSA	24,330	157	500**	18.	1.0	4.2	0.08	0.7	3.9
LFA	13,670	ND	35	28.	5.0	ND	0.04	°°	0.03
PFA	7.930	0.4	18	22.	ND	ND	0.01	6.8	0.1
LAS	14,830	6	40	53.	ND	ND	0.12	5.9	0.5

* The great majority of the metals is lead.

+ Primarily Toluene, trichlorethene, tetrachloroethene, ethylbenezene, xylenes.

° Phthalates, phenols, naphthalene.

¶ ND - not detected

§ Toluene was injected into untreated soil samples for DSA, LFA, and PFA before performing TCLP. Concentration injected equal to level measured in 7 day solids.

** Very high in naphthalene and phenols.

°° Only toluene detected in samples in the range of 0.1 to 28 mg/l.

phenols in the leachates were in the range of hundreds of micrograms per liter, with the same concentration levels seen in both the untreated and treated soil leachates.

PCBs - PCB analyses are in progress and not yet available.

6. The microstructural studies provided the following information:

   The mixing of the four process components was not always complete. At times, microscopic analysis found globules of untreated organics and unreacted cement.

RESULTS - SPECIFIC

The individual results from several test procedures were very interesting. Examples are discussed below:

1. The filter storage area (FSA) had an oil and grease concentration of 25.3%. The unconfined compressive strength (UCS) of the 7 and 28-day FSA samples was many times greater than the laboratory samples made without the proprietary chemical Chloranan.
2. The oil and grease analyses of the untreated waste TCLP leachates were near the detection limits of 0.2 ppm. Oil and grease concentrations ranged from 1 to 25% for the six wastes.

CONCLUSIONS

The following conclusions were drawn from the preliminary analytical data and operations observed at the Douglassville, Pennsylvania Superfund Site:

1. The volume of the solidified soils using the HAZCON process at Douglassville resulted in an increase of approximately 100%, when compared to the volume of the untreated soils,
2. The unconfined compressive strength ranged from 200 to 1500 psi and was inversely proportional to the oil and grease concentration.
3. The TCLP leaching tests for the solidified soils produced very low levels of metals, volatile organics, and semivolatile organics in the leachate. However, for the organics, the leachate concentrations were approximately equal for the treated and untreated soils,

TRANSPORT OF DISSOLVED ORGANICS FROM DILUTE AQUEOUS SOLUTIONS THROUGH FLEXIBLE MEMBRANE LINERS

by: Henry E. Haxo, Jr.
Matrecon, Inc.
Alameda, CA 94501

ABSTRACT

This paper presents the results of experiments relating to the partitioning of dissolved organics from dilute aqueous solutions to polymeric flexible membrane liners (FMLs) and the permeation through FMLs of organics from dilute aqueous solutions. The amount and rate of absorption and the transport of these species through an FML are functions of such factors as their relative solubility parameters, crystallinity content and thickness of the FML, the molecular weight and concentration of the organic constituent, temperature, and their concentration gradients across the liner.

In order to simulate partitioning and the transport of waste constituents within and out of a landfill, two sets of experiments were performed. In the first set, samples of an FML that were either unexposed or saturated with an organic were placed in test liquids, including deionized (DI) water, neat organics, and saturated aqueous solutions of organics; the concentrations at equilibrium were measured. In the second set, the transport of organics in aqueous solutions through an FML was measured in a three-compartment closed apparatus. The distribution of the organics between the test zones in these experiments was monitored by gas chromatography (GC). The results of these experiments show that, even at low concentrations in an aqueous leachate, some organics can be highly absorbed by a polymeric FML and can permeate the liner. A multi-compartment apparatus, such as the one described and used in this work, appears to be an appropriate and promising means of assessing the effectiveness of an FML to contain the organic constituents of a given leachate.

INTRODUCTION

Even though of polymeric flexible membrane liners (FMLs) are recognized for their low permeability to water and waste liquids, their permeability to gases, vapors, and liquids can vary by orders of magnitude (1, 2, 3, 4, 5). The amount and rate at which a constituent of a waste liquid can migrate through an FML and the direction of migration depend on characteristics of the consitituent, the FML, the temperature, and the concentration of the constituent on both sides of the FML. Since polymeric FMLs are nonporous materials, constituents permeate them by a three-step process that involves the solution or absorption of the permeant at the surface of the FML, transport of the permeant through the membrane by diffusion, and evaporation or desorption of the permeant on the downstream side. As a first approximation, the magnitude and the difference in concentration of an individual species across a membrane determine the direction and the driving force for the permeation of that species. Individual organics can permeate an FML at substantially different rates. In a lined-waste disposal facility, an FML generally encounters dilute solutions containing both organic and inorganic species. The individual species can interact with one another and with the FML in different ways, significantly affecting permeation rates of the organic species through the membrane.

This paper begins with a discussion of the concept of partitioning, presents the gas chromatographic procedures and materials used in the experiments, discusses two types of experiments that illustrate the mechanism of transport under conditions that simulate service conditions, and presents the results. These experiments measured:

- The partitioning or distribution of selected organics between water and an FML.
- The transport permeation of selected organics through an FML in a multi-compartment appartus that simulates the configuration of a waste landfill.

PARTITIONING

The distribution of a dissolved substance between two phases that are essentially immiscible has been an important subject for study in chemistry for more than a century (6). Some of the early investigations showed that at equilibrium the ratio of the concentrations of a substance dissolved in two immiscible solvents in contact with one another is constant and does not depend upon the relative volumes of the solutions involved. Later studies showed that the distribution would be constant only if a single molecular species was being considered as being distributed between the two phases, that is, the molecular species would be the same in both phases and would not either dissociate or associate when transferring from one phase to the other. Thus, the partitioning could be treated by classical thermodynamics as an equilibrium process and would be related to other commonly measured functions such as partial pressure, osmotic pressure, and chemical potential. The partitioning of a dissolved substance, for example, between water and an organic such as toluene, forms the basis for the separation of organic compounds by extraction. When there are two or more immiscible phases, an organic solute, for example, will partition or distribute itself among phases depending upon its solubility in the different phases. Many organic solutes will tend to be more soluble in the organic phase and remain in that phase unless the solute is exceptionally soluble in water. Nevertheless, a small amount of the organic will dissolve in water when the two phases are in contact. The ratio at which a solute partitions between the organic and aqueous phases is termed the partitioning or the distribution coefficient and is determined by dividing the concentration of the dissolved substance in the organic phase by its concentration in the aqueous phase.

The concept of partitioning is being used in tracking pollutants and contaminants in the environment, e.g. pesticides and various organics which resist biodegradation, including the polychlorinated biphenyls (PCBs) (7, 8). These chemical species can move through the food chain, resulting in higher concentrations at each trophic level. This process which reflects the greater solubility of an organic chemical in oily tissue than in water has been termed "bioconcentration." The process of partitioning is also involved in spill cleanup processes in which polymeric materials that are used to absorb a spilled organic, e.g. an oil, can then be disposed of in an environmentally safe manner.

In waste disposal containment, a similar situation exists with respect to polymeric FMLs and waste liquids that contain dissolved organic substances. Organics dissolved in waste liquids can partition between the waste liquid and the liner and thus enter and swell the liner. The organic can then permeate and be transported through the liner at a rate which depends on the material, its thickness, the temperature, and the concentration gradient, or more precisely, its "chemical potential" gradient across the liner. Inasmuch as FMLs are organic compounds and are at least partially amorphous, they can behave much like liquids from a thermodynamic standpoint.

The major factors affecting the solubility of a solute in a polymeric composition that is exposed to a liquid are:

o Solubility parameter value of the polymer with respect to that of constituents of the liquid.

- Crosslinking of the polymer.
- Crystallinity of the polymer.
- Filler content of the compound.
- Plasticizer content of the compound.
- Soluble constituents in the compound.

Due to differences in polymers and in compounding, some of these factors do not apply or become important.

For rubber and noncrystalline or amorphous polymers, the solubility parameter is probably the most important factor in swelling and, as noted above, is used by polymer scientists to measure the compatibility of an amorphous polymeric composition with a liquid with which it may be in contact.

Crosslinking of a noncrystalline polymer or a rubber reduces its ability to swell in a liquid which has similar solubility characteristics to the polymer. The amount that a crosslinked polymer swells in a good solvent for the raw polymer can be used to measure the degree of crosslinking: the less the swelling, the greater the crosslinking.

Crystallinity of a polymer acts much like crosslinking to restrict the ability of a polymer to swell and dissolve. The crystalline domains of a polymer do not absorb organics. Highly crystalline polymers, such as HDPE, will swell slightly but will not dissolve in gasoline even though they are both hydrocarbons.

Two additional factors in FML compositions that also can affect the magnitude of swelling of noncrystalline polymers are the amount of filler, e.g. carbon black, silica, or clay, and the amount of plasticizer used in the recipe. As with the crystalline domains in semicrystalline polymers, fillers do not absorb organics. In the latter case the plasticizer is generally extractable by organic solvents, but only slightly extractable by water.

In previous work, Haxo et al (9) observed that slightly soluble organics dissolved in an aqueous waste liquid can partition to an FML which is immersed in the liquid. That work was performed with dilute but saturated aqueous solutions of tri-n-butyl phosphate (TBP) at less than 0.10% concentration, that is, less than 1,000 mg L^{-1}. The weights of FML specimens immersed in a dilute solution of TBP reached an equilibrium. The time required to reach equilibrium depended on the FML and, in some cases, equilibrium was reached after several years. The amount of TBP absorbed at equilibrium also depended on the type of FML. It should be noted that TBP has a molecular weight of 266.3 and a relatively low volatility.

Immersion testing of the FMLs was also performed in neat TBP (10). In that experiment, the absorption of the TBP to equilibrium by various lining materials took place in a relatively short time and, in most cases, ended at considerably higher absorption values than the values in the tests with the saturated solutions, indicating an effect of concentration.

EXPERIMENTAL DETAILS

Two sets of experiments were performed for this study. In the first set, samples of an FML that were either unexposed or saturated with an organic were placed in test liquids, including deionized (DI) water, neat organics, and saturated aqueous solutions of organics. In the second set, the transport of organics in aqueous solutions through an FML was measured in a three-compartment closed apparatus. The distribution of the organics among the test zones was monitored by gas chromatography (GC).

GAS CHROMATOGRAPHY PROCEDURES

A Perkin-Elmer Sigma Three Series gas chromatograph with a flame ionization detector was used for the GC analyses. The instrument was fitted with different columns as required to effect separation of the different mixtures of volatile and semivolatile organics. Different temperature programs for both the oven and the injection/detection ports were also used to maximize separation and response factors for the mixtures. The different conditions, injection volumes, carrier gas flow rates, etc., for each of the experiments are all presented in Table 1.

The concentrations of the organics in the aqueous solutions and the vapor zones of the test apparatus were determined by injecting solution samples directly into the GC column. The experimental apparatuses for exposing the FML samples featured septums through which the liquid and vapor zones could be sampled during the test to determine whether equilibrium had been reached. The concentrations of the organics in the FML samples were determined either by the change in weight of the FML samples or by headspace gas chromatography (HSGC). In the HSGC procedure, an exposed FML specimen is placed in a small vapor-tight can provided with a septum through which vapors from the specimen can be sampled. The can is placed in an oven at 105°C and heated for approximately an hour. A sample of the vapors is drawn from the can and injected into the GC. The FML specimen is removed from the sampled can and placed in a new can which is then heated in a 105°C oven for approximately an hour. Once again, the vapors inside the can are sampled and injected into the GC. The process of heating, sampling, and injecting is repeated until no organics are detected in the sampled vapors by the GC.

The concentrations of the organics in the injected samples were calculated by comparing peak height values with calibration curves. The calibration curves for the leachates were determined by injecting 1 µL of various

TABLE 1. CONDITIONS USED IN GAS CHROMATOGRAPHIC ANALYSES OF LIQUIDS AND VAPORS IN PARTITIONING/PERMEABILITY EXPERIMENTS

Set of conditions	Experiment	Column	Oven temperature program	Injection port and detector temperature (°C)	Injection volume (µL)	Carrier gas (He)[a] flow rate (mL min.$^{-1}$)	O_2/H_2[b] (psi)
1	Polyethylene specimens saturated with organics and placed in water	6 ft x 1/8 in. SS; 10% Carbowax 20M on 80/100 mesh Supelcoport	60°C for 1 min. to 140°C at 20°C/min.	250	Liquid: 1; Vapor: 400	30	40/30
2	Three-compartment apparatus with water spiked with TCE and toluene	DB WAX-1, 15M, polyethylene glycol, fused silica open tube (FSOT)	60° to 160°C at 20°C/min.	275	Liquid: 1; Vapor: 100	8	40/30
3	Three-compartment apparatus with water spiked with six organics	DB WAX-1, 15M, polyethylene glycol, fused silica open tube (FSOT)	60° to 160°C at 20°C/min.; 2 min. at 160°C	275	Liquid: 1; Vapor: 100	8	40/30

[a] Pre-purified helium passed through an oxygen trap.

[b] USP-grade oxygen used to burn the reagent-grade hydrogen in the flame-ionization detector.

solutions of known concentrations of the different organics into the GC column. Injections of each standard were performed five times to ensure reproducibility of injection techniques. Standard deviation was 2%. The calibration curves for the HSGC analyses were prepared by analyzing a specific volume of vapor (either 100 μL or 400 μL) from headspace cans injected with different volumes of a standard solution of organics.

ORGANICS USED IN EXPERIMENTS

Basic information for the organics used in these experiments is presented in Table 2.

TABLE 2. ORGANICS USED IN PARTITIONING/PERMEABILITY EXPERIMENTS

Organic	Molecular weight	Density at 20°C (g cm^{-3})	Boiling point (°C)	Vapor pressure at 25°C (mm Hg)	Solubility parameters[a]				Solubility in water (mg L^{-1})[b]
					(δ_o)	(δ_d)	(δ_p)	(δ_h)	
Aliphatic hydrocarbon									
n-Octane	114.23	0.703	125.7	16.71	7.6	7.6	0.0	0.0	6.6
Aromatic hydrocarbons									
Benzene	78.11	0.879	80.1	96.43	9.2	9.0	0.0	1.0	1,178
Toluene	92.13	0.866	110.6	31.96	8.9	8.8	0.7	1.0	515
o-Xylene	106.16	0.897	144.0	8.22	8.8	8.7	0.5	1.5	175
m-Xylene	106.16	0.868	139.3	9.15	8.6	8.4	0.5	1.2	196
p-Xylene	106.16	0.854	137-138	9.41	8.6	8.4	0.5	0.1	190
Chlorinated hydrocarbons									
1,1,1-Trichlorethane	133.42	1.338	74.1	143.35	8.6	8.3	2.1	1.0	1,320
Trichloroethylene	131.40	1.476	87.2	80.30	9.2	8.8	1.5	2.6	1,100
Oxygenated hydrocarbons									
Propionic acid	74.08	0.993	141.1	6.23	12.4	7.5	5.5	8.4	∞
Acetone	58.08	0.788	56.5	263.2	9.9	7.6	5.1	3.4	∞
Methyl ethyl ketone	72.10	0.805	79.6	100.0	9.3	7.8	4.4	2.5	240,000
n-Butyl alcohol	74.12	0.810	117.7	8.50	11.3	7.8	2.8	7.7	74,500
n-Butyric acid[c]	88.11	0.964	162.0	1.00	10.5	7.3	2.0	5.2	∞

[a] Barton (11).
[b] Riddick and Bunger (12).
[c] n-Butyric acid observed in the partitioning experiment was the oxidation product of n-butanol.

FMLS USED IN EXPERIMENTS

Selected property values of the two FMLs used in these experiments are presented in Table 3.

TABLE 3. SELECTED PROPERTIES OF POLYETHYLENE FMLS USED IN STUDY

Polymer[a]	LLDPE	HDPE
FML number[b]	284	483
Nominal thickness (mil)	30	100
Volatiles (%)	...	0.1
Carbon black content (%)	2.5	2.5
Specific gravity of FML	0.927	...
Density at 23°C		
FML (g mL^{-1})	0.924	0.945
Polyethylene[c] (g mL^{-1})	0.913	0.936
Crystallinity (%)	36.3	59
Melting point (°C)	119	121

[a] LLPE = linear low-density polyethylene; HDPE = high-density polyethylene.
[b] Matrecon identification number.
[c] Calculated from the density of the FML by correcting for the carbon black content.

DISTRIBUTION OF ORGANICS BETWEEN WATER AND AN FML

In the first set of experiments, samples of an FML were placed in the test liquids to determine the distribution of a selected group of organics between water and an FML. The FML samples that were placed in the test liquids were either unexposed or saturated with an organic. The unexposed samples were placed in saturated aqueous solutions of the respective organic, and the samples saturated with organics were placed in DI water.

DISTRIBUTION OF ORGANICS BETWEEN ORGANIC-SATURATED WATER AND A POLYETHYLENE FML

To assess the distribution of dissolved organics between an aqueous solution and an FML, a series of saturated aqueous solutions, each containing a single organic, were prepared with an excess of organics and placed in vapor-tight jars. Since acetone, which was in this series, is miscible with water at all proportions, the aqueous solution was prepared at 250,000 mg of acetone per liter (L) of solution.

A specimen of polyethylene FML (No. 483) was immersed in each jar. At intervals, each immersed specimen was removed and weighed until it reached a maximum value; the concentration of the organic in the FML specimen was calculated and reported in mg of organic per L of solution, i.e. per L of FML. The values used for the concentrations of the organics in the saturated aqueous solutions were obtained from the literature (12). The distribution coefficients (D_{LW}), i.e. the ratio of the concentration of the organic in the FML (C_{FML}) to the concentration in the aqueous solution (C_{H_2O}), were calculated. The results of the analyses and calculations are presented in Table 4.

TABLE 4. DISTRIBUTION OF NINE ORGANICS BETWEEN SATURATED AQUEOUS SOLUTIONS AND A POLYETHYLENE FML[a]

Organic	Density of organic (g mL^{-1})	Solubility in water at room temperature[b] (C_{H_2O}) (mg L^{-1})	Time to maximum swelling (days)	Weight increase of HDPE FML specimen (%)	Concentration of organic in swollen FML (C_{FML}) (mg L^{-1})	Distribution coefficient (D_{LW}) (C_{FML}/C_{H_2O})
Acetone	0.788	250,000[c]	44	0.33	3,210	0.0128
Methyl ethyl ketone	0.805	240,000	46	0.62	5,900	0.0246
Trichloroethylene	1.464	1,100	43	16.71	144,200	131.0
1,1,1-Trichloroethane	1.339	1,320	52	11.70	103,000	78.2
Benzene	0.879	1,180	30	7.22	63,900	54.3
Toluene	0.866	515	50	8.05	70,600	137
o-Xylene	0.897	175	40	8.42	73,800	422
m-Xylene	0.868	196	38	8.19	71,800	366
p-Xylene	0.854	190	49	8.43	73,600	387

[a] HDPE FML (No. 483).
[b] Values obtained from Riddick and Bunger (12).
[c] Initial concentration of the acetone-water solution; acetone is miscible with water in all proportions.

In all cases, more than 30 days were required for the specimen to reach maximum swelling. The time required to reach maximum swelling ranged from 30 days for the specimen immersed in benzene solution to 52 days for the specimen immersed in the TCE solution. The distribution of all of the organics, except the acetone and MEK, was predominantly to the HDPE specimens. The distribution coefficients ranged from 54 for benzene to 422 for o-xylene.

DISTRIBUTION OF ORGANICS BETWEEN A SATURATED POLYETHYLENE FML AND DEIONIZED WATER

In this experiment, individual specimens of the same polyethylene FML (No. 483) were saturated with each of the organics. These specimens, approximately 1 x 3 in. in size and 2 g in weight, were immersed in the respective organics and weighed daily until equilibrium was reached. Once the specimens were saturated, they were immersed in vapor-tight jars filled with DI water. The vapor-tight jars consisted of 8-oz glass jars with ground and polished-top edges, and Teflon-lined phenolic resin tops, each of which was fitted with a Swagelock sampling port and Teflon-lined silicone rubber septums (Figure 1). The water in each jar was sampled periodically and analyzed by GC for the organic that transferred from the saturated FML specimen. The water was sampled with a 1-μL syringe initially at 5-min. intervals and then hourly. Concentrations in these tests were determined in the GC under Set of Conditions 1 as described in Table 1. This procedure was continued until the concentration of the organic in the water had plateaued, at which time the specimen was withdrawn and weighed. The concentration of the organic remaining in the FML specimen was determined by HSGC.

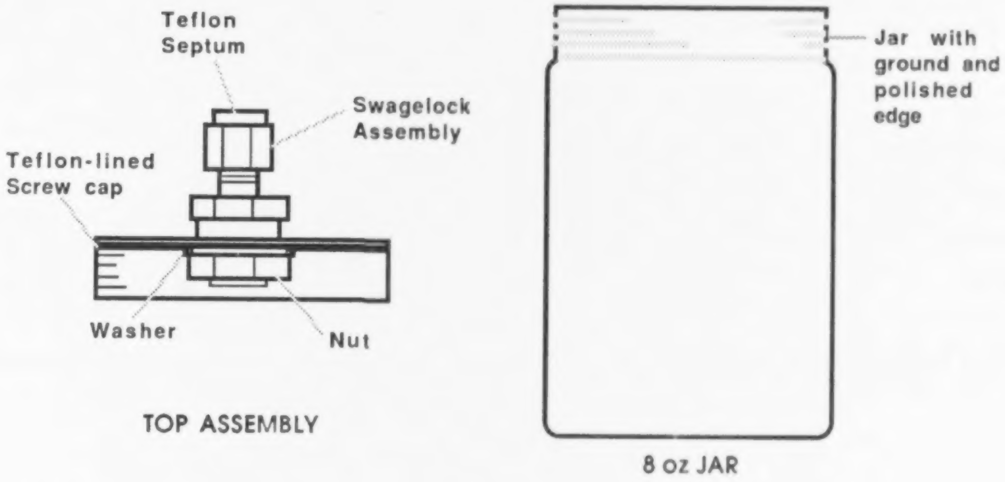


Figure 1. Schematic of the immersion test jar with septum for withdrawing samples of water for GC analysis.

Data on the weight at maximum swelling of the specimens at saturation as well as the weights of the swollen specimens after equilibrating with the water in the jars, and the time required for each to reach equilibrium are presented in Table 5. The rates at which the absorbed organics diffused out of the FML into the water varied considerably. It took 24 hours for the water containing the specimen swollen with TCE to reach equilibrium concentration, whereas the water containing the specimen swollen with benzene required 120 hours. It does not appear that equilibrium had been reached with acetone and MEK when the specimens were withdrawn.

TABLE 5. DISTRIBUTION OF ORGANICS BETWEEN AN ORGANIC SATURATED FML[a] AND DEIONIZED WATER

	Saturated FML		At equilibrium in deionized water				
Organic	Maximum swelling, by weight (%)	Concentration of organic (mg L^{-1})	Time to maximum concentration in H_2O (hours)	Swelling of FML, by weight (%)	Concentration of organic in FML (C_{FML}) (mg L^{-1})	Concentration of organic in water (C_{H_2O}) (mg L^{-1})	Distribution coefficient (D_{LW}) (C_{FML}/C_{H_2O})
Acetone	0.96	9,080	~120[b]	0.62	5,830	35	167
Methyl ethyl ketone	1.83	17,120	~120[b]	0.91	8,990	127	71
Trichloroethylene	17.52	150,500	24	8.98	84,800	966	88
1,1,1-Trichloroethane	12.13	106,700	50	6.91	65,800	589	112
Benzene	7.61	67,100	120	1.95	19,030	643	30
Toluene	8.40	73,400	46	4.42	42,000	266	158
o-Xylene	8.73	76,300	52	7.07	65,600	186	352
m-Xylene	8.51	74,300	78	6.70	62,200	193	322
p-Xylene	8.72	75,900	58	6.93	64,300	165	390

[a] HDPE FML (No. 483).
[b] Equilibrium did not appear to have been reached when specimen was removed from test at 120 hours.

The distribution coefficients, also presented in Table 5, show the strong tendency of the chlorinated and aromatic organics to remain in the polyethylene FML (No. 483).

DISTRIBUTION OF ORGANICS IN A TEST APPARATUS CONSISTING OF THREE COMPARTMENTS SEPARATED BY POLYETHYLENE FMLS

The experiments initially performed in an apparatus consisting of two compartments separated by an FML demonstrated the feasibility of this type of apparatus in assessing the transmission of organics from dilute aqueous solutions through polymeric FMLs. In these experiments, the transmission of specific organics was monitored by GC (13). These experiments also indicated the substantial differences in solubility of different organics in a polymeric FML.

THREE-COMPARTMENT TEST APPARATUS

In order to assess the permeation of organics from dilute aqueous solution through polymeric FMLs under conditions that simulate service conditions for an FML, a three-compartment closed apparatus was fabricated. The test apparatus, shown schematically in Figure 2, can be divided into seven zones, which are listed in Table 6. FML specimens separate the three compartments (Zones 2 and 5). An aqueous solution containing organics partially fills the middle compartment (Zone 4), and DI water can be placed

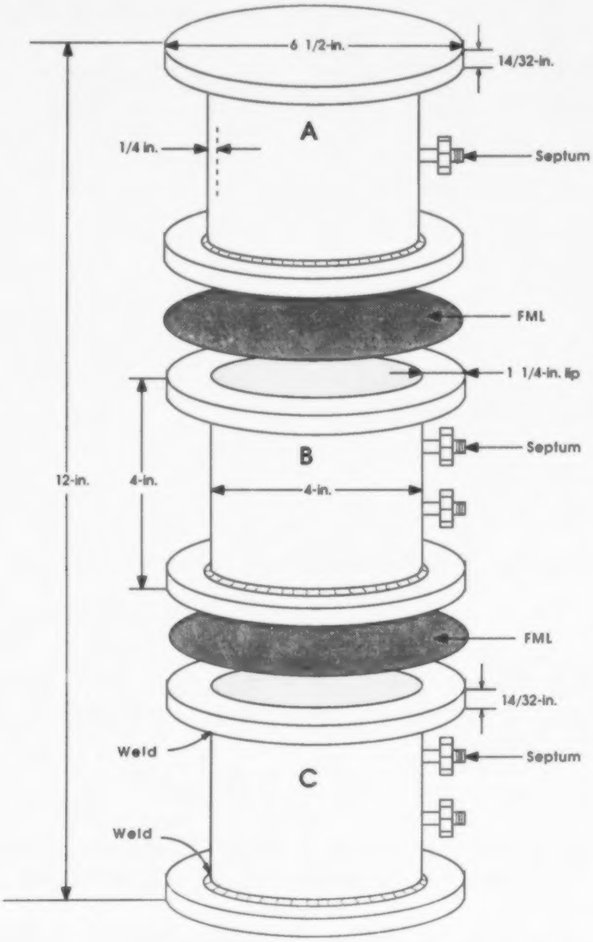

6 1/2-in.
14/32-in.
A
1/4 in.
Septum
FML
1 1/4-in. lip
B
Septum
12-in.
4-in.
4-in.
FML
14/32-in.
Weld
C
Septum
Weld

Figure 2. Schematic of the three-compartment test apparatus used in the study of water/FML distribution and permeation of organics from dilute solutions. Inside diameter of the compartment was 4 inches.

TABLE 6. ZONES IN THREE-COMPARTMENT TEST APPARATUS

Zone	Compartment	Description	Volume (mL)
1	Top	Airspace above "cover"	806
2	Barrier between top and middle	"Cover" FML (33-mil LLDPE): Area exposed to solution	~7
3	Middle	Airspace above aqueous solution containing organics	306
4	Middle	Dilute aqueous solution containing organics	500
5	Barrier between middle and bottom	"Bottom liner" (33-mil LLDPE): Area exposed to solution	~7
6	Bottom	Airspace below "bottom liner" FML	506
7	Bottom	Deionized water	300
		Total	2,432

in the bottom compartment (Zone 7). The three compartments are clamped tightly together to prevent leakage of any vapor from the apparatus. Thus, the organics can either volatilize into the airspace above the solution and then, permeating through the top FML specimen, enter the top compartment or the organics can permeate through the lower FML specimen and into the bottom compartment. The covers of one end of each of the top and the bottom compartments are welded to the walls to prevent loss of volatiles. The only potential leaks are those that might occur at the flanges between which the FML specimens are mounted. Ports with Teflon silicone rubber septums are incorporated in each of the three compartments for use in withdrawing samples for GC analysis from the aqueous and airspace zones. The two FML zones can be analyzed by HSGC after the apparatus is dismantled.

The three-compartment apparatus simulates the configuration of a covered landfill as follows:

- The airspace in the top compartment simulates the airspace over a "cover" liner. The FML specimen between the top and middle compartments simulates a "cover" liner.

- The airspace in the middle compartment simulates the headspace above a waste liquid, and the dilute solution containing organics serves as the waste liquid. The FML specimen between the middle and bottom compartments simulates the service conditions of a single bottom liner.
- The airspace and the deionized water in the bottom compartment simulate, respectively, pore space in the soil and the groundwater.

The configuration of the zones within each compartment can be modified to assess double liners and various auxiliary materials, such as soil covers, geotextiles, and drainage materials.

DISTRIBUTION OF TWO ORGANICS IN TEST APPARATUS

In the first experiment of this series, toluene and TCE were dissolved in the water in the middle compartment. Both of these organics are commonly found in leachates and are easily identifiable and trackable by GC analysis. An LLDPE FML (No. 284) separated the three compartments.

In this experiment, Zone 4 was filled with 500 mL DI water and spiked with 191 mg each of toluene and TCE to yield concentrations of 382 mg each per L of water. The five zones containing water or vapor were sampled and analyzed by GC periodically to assess the changes in concentrations in these zones. After 256 hours, when the concentrations appeared to remain constant, the apparatus was dismantled and the FML samples were removed and analyzed by HSGC to determine the concentrations of the organics in the FMLs. The conditions of the GC analyses are presented in Table 1 (Set of Conditions 2). The results of analyzing the samples taken at 24, 96, and 256 hours are reported in Table 7.

The results show that the water in the bottom compartment (Zone 7) had absorbed organics. At the end of the test, the relative concentrations of the two organics were the same in both aqueous zones (Zones 4 and 7), demonstrating the transport of these organics through the FML and airspace to the water at the bottom. The data also show that, for each of the two organics, the concentrations in the airspaces (Zones 1, 3, and 6) were similar in value and the concentrations in the two FML specimens were essentially equal. Overall, 92.6% of the TCE and 97.7% of the toluene were accounted for in the final analyses of all zones. The HSGC analysis of the FML in the flange area showed no organics, which indicated that there was no leakage through the flanges. Overall, these results show that the apparatus had come to equilibrium; they also show the high absorption of the two organics by the FML. At these equilibrium conditions, the distribution coefficients between the LLDPE FML and water for TCE and toluene were 178 and 120, respectively.

TABLE 7. DISTRIBUTION OF TCE AND TOLUENE IN THREE-COMPARTMENT TEST APPARATUS SEPARATED BY POLYETHYLENE FMLS

Zone				Start of test		At 24 hours		At 96 hours		At end of test (256 hours)	
No.	Description	Volume (mL)	Organic	Amount (mg)	Concentration (mg L^{-1})	Amount (mg)	Concentration (mg L^{-1})	Amount (mg)	Concentration (mg L^{-1})	Amount (mg)	Concentration (mg L^{-1})
1	Airspace above "cover" FML[b]	806	TCE[a]	0	0	9.2	11.5	14.1	17.5	12.9	16.0
			Toluene	0	0	7.9	9.8	10.0	12.5	4.8	6.0
2	"Cover" polyethylene FML[b]	7.02	TCE	0	0	...	...	...	...	56.1	7,991
			Toluene	0	0	...	...	...	...	60.2	8,575
3	Airspace above test liquid	306	TCE	0	0	12.1	39.5	8.8	29.0	5.97	19.5
			Toluene	0	0	10.1	33.0	8.1	26.5	1.83	6.0
4	Test liquid	500	TCE	191	381	95	190	80	160	22.5	45.0
			Toluene	191	381	92	185	80	160	35.7	71.4
5	Barrier FML[b]	7.02	TCE	0	...	...	...	...	...	56.1	7,991
			Toluene	0	...	...	...	...	...	60.2	8,575
6	Airspace below FML	506	TCE	0	...	8.6	17.2	11.9	23.5	9.87	19.5
			Toluene	0	...	1.16	2.3	3.74	7.4	2.58	5.1
7	"Groundwater"	300	TCE	0	...	0.75	1.5	6.42	21.4	13.5	45.0
			Toluene	0	...	0	0	4.57	15.2	21.4	71.4
	Total	2,432	TCE	191	381	125.6	...	121	...	176.9	...
			Toluene	191	381	111.1	...	106.4	...	186.7	...
	Fraction accounted for, %		TCE	100		65		63		92.6	
			Toluene	100		58		55		97.7	

[a] Trichloroethylene.

[b] Linear low-density polyethylene FML (No. 284).

DISTRIBUTION OF SIX ORGANICS IN TEST APPARATUS

In another experiment performed with the same type of test apparatus, same configuration of zones, and same polyethylene FML (No. 284), 191 mg each of six organics were injected into the 500 mL of water in the middle compartment in Zone 4; the organics included n-octane, TCE, toluene, o-xylene, n-butanol, and propionic acid. Table 2 presents data on these organics. Due to the low solubility of n-octane in water, the amount of this organic added to the water was excessive.

The five zones that contained either liquid or vapor were monitored by sampling and analysis by GC. Exposure in the test apparatus was continued until essentially no change took place in the concentrations of these chemicals in any given zone. At 28 days, the analyses indicated that concentrations of the toluene and TCE had reached equilibrium, at which time the test apparatus was dismantled and the FMLs were analyzed by HSGC for the organics that they had absorbed. The conditions for the GC analyses are presented in Table 1 (Set of Conditions 3). The results, which include concentration data for 24 hours, 96 hours, and 28 days, are presented in Table 8.

All of the organics, except the n-butanol, could be followed throughout the exposure and appeared in different zones of the test apparatus in the final analyses performed after 28 days of exposure. Seventy-five to 85% of the aliphatic, aromatic, and chlorinated hydrocarbons, and 57% of the propionic acid were accounted for in the final analyses. The n-butanol, which was injected into Zone 4 at the beginning of the test, was not detected after about a week and appeared to be replaced by n-butyric acid which was detected by GC analysis. Based on a total conversion of n-butanol to n-butyric acid, 11.5% of the n-butanol was accounted for as n-butyric acid in the final analyses. A portion of the apparent loss of the organics can probably be attributed to the large number of samples withdrawn from the test apparatus during the 28 days of exposure for GC analysis to track the organics.

The distribution and transport of each of the organics that were initially placed in the water in Zone 4 are discussed briefly in the following subsections.

n-Octane

The n-octane was injected at a concentration substantially above its solubility in water. It appeared within 24 hours in the airspace above the spiked water and was substantially absorbed by the upper FML. In the final analysis, essentially 75% of the spike was concentrated in the upper FML, a small amount was detected in the lower FML, and the remainder was observed in the airspaces, particularly in the upper airspace (Zone 1). Only a trace amount was found in the liquid in the bottom compartment.

TABLE 8. DISTRIBUTION OF ORGANICS FROM A DILUTE AQUEOUS SOLUTION IN TEST APPARATUS CONSISTING OF THREE-COMPARTMENTS SEPARATED BY POLYETHYLENE FML BARRIERS

Zone				Start of test		At 24 hours		At 96 hours		At end of test, 28 days	
No.	Description	Volume (mL)	Organic	Amount (mg)	Concentration (mg L^{-1})	Amount (mg)	Concentration (mg L^{-1})	Amount (mg)	Concentration (mg L^{-1})	Amount, (mg)	Concentration, (mg L^{-1})
1	Airspace above "upper" FML	806	n-Octane	0	0	12.1	15	4.8	6	2.58	3.2
			Trichloroethylene	0	0	8.1	10	12.5	15.5	19.3	24.0
			Toluene	0	0	28.3	35.1	8.1	10.0	5.64	7.0
			o-Xylene	0	0	10.7	13.3	4.8	6	4.19	5.2
			Propionic acid	0	0	-----none-----		-----none-----		------none------	
			n-Butanol	0	0	-----none-----		-----none-----		------none------	
2	"Upper" polyethylene FML[a]	7.02	n-Octane	0	0	Analyzed by headspace GC when the apparatus was dismantled				126.7	18,051
			Trichloroethylene	0	0					37.8	5,885
			Toluene	0	0					49.3	7,024
			o-Xylene	0	0					76.0	10,829
			Propionic acid	0	0					------none------	
			n-Butanol	0	0					------none------	
3	Airspace above spiked water	306	n-Octane	0	0	20.8	68.0	18.7	61	0.98	3.2
			Trichloroethylene	0	0	12.2	40	4.90	16	6.23	20.1
			Toluene	0	0	11.3	37	3.21	10.5	2.14	7.0
			o-Xylene	0	0	2.1	6.8	1.04	3.4	1.59	5.2
			Propionic acid	0	0	-----none-----		-----none-----		------none------	
			n-Butanol	0	0	-----none-----		-----none-----		------none------	
4	Spiked water	500	n-Octane	191	382	0.3	0.6	0.3	0.6	0.3	0.6
			Trichloroethylene	191	382	40.1	80	20.0	40	17.1	34.2
			Toluene	191	382	48.1	96	22.5	45	15.0	30.0
			o-Xylene	191	382	----trace-----		----trace-----		0.5	1
			Propionic acid	191	382	106	212	102	204	99.7	199.5
			n-Butanol	191	382	140	280	110	220	------none------	
			n-Butyric acid[b]	0	0	-----none-----		----trace-----		20.75	41.25
5	"Lower" polyethylene FML[a]	7.02	n-Octane	0	0	Analyzed by headspace GC when apparatus was dismantled				2.60	370
			Trichloroethylene	0	0					47.60	6,780
			Toluene	0	0					61.15	8,712
			o-Xylene	0	0					76.04	10,833
			Propionic acid	0	0					------none------	
			n-Butanol	0	0					------none------	
6	Airspace below "lower" FML	506	n-Octane	0	0	-----none-----		1.36	2.7	1.29	2.56
			Trichloroethylene	0	0	0.4	0.8	2.6	5.2	14.2	28.2
			Toluene	0	0	0.3	0.6	3.8	6.5	5.0	10.0
			o-Xylene	0	0	0.03	0.015	0.126	0.25	1.9	3.75
			Propionic acid	0	0	-----none-----		-----none-----		------none------	
			n-Butanol	0	0	-----none-----		-----none-----		------none------	
7	Bottom water	300	n-Octane	0	0	-----none-----		----trace-----		------trace------	
			Trichloroethylene	0	0	0.15	0.5	4.23	14.1	20.58	68.6
			Toluene	0	0	-----none-----		0.468	1.56	5.6	18.75
			o-Xylene	0	0	-----none-----		-----none-----		------none------	
			Propionic acid	0	0	-----none-----		----trace-----		10.1	33.15
			n-Butanol	0	0	-----none-----		-----none-----		------none------	
			n-Butyric acid[b]	0	0	-----none-----		----trace-----		5.4	18.0
										Total in all zones[c]	
			n-Octane	191						155.03	(81.0)
			Trichloroethylene	191						162.8	(85.2)
			Toluene	191						143.8	(75.3)
			o-Xylene	191						160.2	(83.9)
			Propionic acid	191						109.8	(57.4)
			n-Butanol	191						0	(0)
			n-Butyric acid[b]	0						26.15	(11.5)

---

[a] Linear low-density polyethylene FML (No. 284).

[b] n-Butanol appeared to have been oxidized to n-butyric acid which was detected in the GC as the amount of n-butanol detected in the closed apparatus decreased.

[c] Data in parentheses are the percent of initial organics accounted for in the final analysis.

The n-octane did not migrate downwards into the lower FML and into the airspace below the FML because of its low solubility in water. The absorption of the n-octane by the upper FML is attributed to its solubility in the FML, both of which have essentially the same solubility parameter value.

Trichloroethylene

The spike of the trichloroethylene (TCE) was approximately 1/3 of the solubility of TCE in water. Due to its volatility, the TCE was observed quickly in the space above the spiked water in Zone 4 and also in the airspace above the upper FML. In the final analysis, the TCE was present in all zones, although approximately 50% of that measured was in the FMLs; a substantial amount was transported into the liquid in the bottom compartment.

These results show the tendency of the TCE to migrate and to be transported through all phases and reflect the solubility of TCE in water as well as in FMLs. At the end of the test, of the six organics in the study, the TCE had the highest concentration in the water in the bottom compartment. The results indicate that special efforts are needed to control this organic.

Toluene

The amount of toluene injected into the water in Zone 4 was below its solubility level in water. Toluene behaved similarly to the TCE, although it did not migrate as rapidly. However, it was in the airspace above the upper FML in essentially the same concentration as the TCE. As with the TCE, only a small quantity of the toluene was present (0.3 mg) below the lower FML at the end of 24 hours.

At the time of dismantling, the toluene was present in all seven zones, with approximately 77% of the total in the two FML layers. As with the TCE, it moved through all zones of the test apparatus. The results indicate that special efforts are needed to control this organic.

o-Xylene

The amount of o-xylene injected into the water in Zone 4 was approximately twice its solubility level in water, i.e. 382 vs. 175 mg L^{-1}, and it was anticipated that the o-xylene would tend to migrate relatively rapidly. The o-xylene appeared to have left Zone 4 quickly; it was detected at significant concentrations (up to 13 mg L^{-1}) in the airspaces after 24 hours; only a trace was detected in the water in Zone 4, and none in the water in the bottom compartment.

In the final analyses, the o-xylene was concentrated principally in the FMLs; almost all of it had migrated out of the spiked water. Also, the concentration in the airspaces was low in comparison with that in the FMLs, which demonstrates the strong affinity of the o-xylene for the FML and reflects its comparatively low solubility in water.

Propionic Acid

Propionic acid has a high solubility parameter value and is completely miscible with water; therefore, it has a strong affinity for water. Only 57% of the propionic acid that was injected at the beginning of the experiment was accounted for in the final analyses; approximately 75% of that was still in the spiked water and the remainder was detected in the water in the bottom compartment. No propionic acid was detected in the other zones of the test apparatus.

n-Butanol

After the first few days of analyses, no n-butanol was observed in any of the zones. However, n-butyric acid appeared in the analyses, indicating that the n-butanol had been oxidized to n-butyric acid. No butyl propionate appeared in the GC scan; thus, the possibility of esterification of the n-butanol with the propionic acid could be discounted. Assuming that the n-butanol was completely converted to n-butyric acid, 11.5% would have been accounted for as n-butyric acid which was detected only in the aqueous phases.

During the dismantling of the test apparatus, there was considerable pressure in the bottom compartment, which may have been CO_2 generated from the decomposition of the acids; CO_2 cannot be detected by flame-ionization detection in the GC. Also, the bottom compartment fabricated of aluminum exhibited some corrosion and darkening of the surface.

DISCUSSION

The experiments on the distribution of volatile organics from dilute aqueous solutions show that, even at low concentrations, some organics can be highly absorbed by a polymeric FML and can permeate the liner. Table 9 compares the swelling of an HDPE FML in a series of neat organics with the swelling of the same FML in a series of saturated aqueous solutions of the same organics. These results show that the amount of organic that an FML can absorb during exposure to a saturated aqueous solution of an organic can approach the amount an FML can absorb during exposure to a neat organic. Even though the maximum swelling values for the specimens exposed to the neat organics were all somewhat higher, the maximum swelling values obtained in the neat organics were approximately equal to those obtained in the saturated dilute solutions.

TABLE 9. COMPARISON OF THE SWELLING OF A POLYETHYLENE FML[a] IMMERSED IN NEAT ORGANICS AND IN SATURATED AQUEOUS SOLUTIONS OF ORGANICS

Organic	Neat organic		Saturated aqueous solution	
	Maximum swelling, by weight (%)	Time to maximum swelling (days)	Maximum swelling, by weight (%)	Time to maximum swelling (days)
Acetone[b]	0.96	18	0.33	44
Methyl ethyl ketone	1.83	21	0.62	46
1,1,1-Trichloroethane	12.13	17	11.70	52
Trichloroethylene	17.52	15	16.71	43
Benzene	7.61	6	7.22	30
Toluene	8.40	6	8.05	50
o-Xylene	8.73	9	8.42	40
m-Xylene	8.51	6	8.19	38
p-Xylene	8.72	7	8.43	49

[a] HDPE FML (No. 483).

[b] Acetone is miscible with water in all proportions; the concentration was set at 250,000 mg L^{-1} for the experiment with the aqueous solution.

However, the results presented in Table 9 also show that the time to reach maximum swelling values can be significantly affected by the concentration of the organic in the liquid in contact with the FML. The specimens exposed to the neat organics reached maximum swelling values in considerably shorter times than the specimens exposed to the saturated aqueous solutions.

The results of determining the distribution of organics between saturated FML specimens and DI water indicate that the concentration of an organic in an in-service FML is affected by the concentration of the organic in the liquid in direct contact with the FML and that the concentration of the organic in the FML will change as the concentration of the organic in the liquid in contact with the FML changes.

The results of measuring the distribution of organics in the different zones of a multi-compartment apparatus indicate that the amount and rate of absorption and the transport of these species through a polymeric FML is a function of such factors as relative solubility parameters of the FML and the organic, crystallinity of the FML, and molecular weight and concentration of the organic constituent. A multi-compartment apparatus, such as the one described and used in this work, appears to be an appropriate and promising means of assessing the effectiveness of an FML to contain the organic constituents of a given leachate.

REFERENCES

1. August, H., and R. Tatzky. Permeabilities of Commercially Available Polymeric Liners for Hazardous Landfill Leachate Organic Constituents. In: Proceedings of the International Conference on Geomembranes, June 20-24, 1984, Denver, CO. Vol. I. Industrial Fabrics Association International, St. Paul, MN, 1984. pp 163-168.

2. Haxo, H. E., and N. A. Nelson. Permeability Characteristics of Flexible Membrane Liners Measured in Pouch Tests. In: Proceedings of the Tenth Annual Research Symposium: Land Disposal of Hazardous Waste. EPA-600/9-84-007, U.S. Environmental Protection Agency, Cincinnati, OH, 1984. pp 230-251.

3. Haxo, H. E., J. A. Miedema, and N. A. Nelson. Permeability of Polymeric Membrane Lining Materials. In: Proceedings of the International Conference on Geomembranes, June 20-24, 1984, Denver, CO. Vol. I. Industrial Fabrics Association International, St. Paul, MN, 1984. pp 151-156.

4. Haxo, H. E., J. A. Miedema, and N. A. Nelson. Permeability of Polymeric Lining Materials for Waste Management Facilities. In: Migration of Gases, Liquids, and Solids in Elastomers. Education Symposium. Fall Meeting - Denver, CO. Rubber Division, American Chemical Society. The John H. Gifford Memorial Library and Information Center, The University of Akron, Akron, OH, 1984.

5. Matrecon, Inc. Lining of Waste Impoundment and Disposal Facilities. SW-870 Revised, U.S. Environmental Protection Agency, Washington, D.C., 1983. 448 pp. GPO #05500000231-2.

6. Leo, A., C. Hansch, and D. Elkins. Partition Coefficients and Their Uses. Chemical Reviews 71(6):525-554, 1971.

7. Neely, W. B., D. R. Branson, and G. E. Blau. Partition Coefficient to Measure Bioconcentration of Potential Organic Chemicals in Fish. Environ. Sci. Technol. 8(13):1113-1115, 1974.

8. Chiou, C. T. Partition Coefficient and Water Solubility in Environmental Chemistry. In: J. Saxena and F. Fisher (eds.), Hazard Assessment of Chemicals, Current Developments. Vol. 1. Academic Press, NY, 1981. pp 117-153.

9. Haxo, H. E., R. S. Haxo, N. A. Nelson, P. D. Haxo, R. M. White, and S. Dakessian. Liner Materials Exposed to Hazardous and Toxic Wastes. EPA-600/2-84-169, U.S. Environmental Protection Agency, Cincinnati, OH, 1985. NTIS No. PB 85-121-333.

10. Haxo, H. E., N. A. Nelson, and J. A. Miedema. Solubility Parameters for Predicting Membrane-Waste Liquid Compatibility. In: Proceedings of the Eleventh Annual Research Symposium: Land Disposal of Hazardous Waste. EPA/600/9-85/013, U.S. Environmental Protection Agency, Cincinnati, OH, 1985. pp 198-212.

11. Barton, A.F.M. Solubility Parameters and Other Cohesion Parameters Handbook. CRC Press, Boca Raton, FL, 1983. 594 pp.

12. Riddick, J., and W. Bunger. Techniques of Chemistry. Volume II - Organic Solvents, Physical Properties and Methods of Purification. Wiley-Interscience, NY, 1970.

13. Haxo, H. E., T. P. Lahey, and M. L. Rosenberg. Factors in Assessing the Compatibility of FMLs and Waste Liquids. Contract No. 68-03-3213, U.S. Environmental Protection Agency, Cincinnati, OH, 1987. 143 pp. (In press).

THE ELECTRICAL LEAK LOCATION METHOD FOR GEOMEMBRANE LINERS

by: Glenn T. Darilek
Jorge O. Parra
Southwest Research Institute
San Antonio, Texas 78284

ABSTRACT

An electrical method for locating leaks in geomembrane liners was developed and demonstrated for a wide variety of applications. Geomembrane liners are sheets of elastomeric material used to prevent the leakage of waste and to prevent rainwater from infiltrating landfills and surface impoundments. When no leaks are present, a voltage applied between the material in the liner and the earth under the liner produces a relatively uniform electrical potential distribution in the material in the liner. Leaks are located by mapping any anomaly in the potential distribution caused by current flowing through a leak. A computer simulation model of layered earth sequences above and below an insulating liner with a leak was developed to predict efficiently the effect of a wide range of parameters on the leak signature.

Tests on a double-lined physical model demonstrated the applicability of the method to a variety of drainage layers with various test parameters such as leak size, electrode depth, and protective cover soil. Leaks with a diameter smaller than 0.8 millimeters in the primary liner were reliably located to within 10 millimeters. Leaks in the bottom liner could be detected, but not located. The electrical leak location method was successful in finding leaks in a full-scale impoundment that had been fully tested using the vacuum box method.

The electrical leak location method was adapted for locating leaks in the geomembrane liner of landfill cover systems. Scale model tests demonstrated the applicability of the method under a wide range of cover soil thicknesses and leak sizes. Special non-polarizing electrodes were used to locate leaks with diameters as small as 3 millimeters under 600 millimeters of cover soil.

INTRODUCTION

The most common method of disposal of solid and hazardous wastes is in landfills and surface impoundments. To prevent contamination, double geomembrane liner systems are installed beneath the landfill or impoundment to form an essentially impermeable barrier that prevents the migration of contaminant liquids. Geomembrane liner material is used for landfill final cover systems to prevent rainwater from percolating through the waste and leaching chemicals that could migrate into groundwater or surface water.

Installation practices and operational factors can result in leaks in the form of punctures or separated seams. An electrical leak location method was developed to effectively locate leaks in geomembrane liners to ensure that liners have been installed and seamed properly and that the integrity of the containment system is maintained.

The electrical leak location method can be used in liquid impoundments, as a pre-service inspection of solid waste landfills, and to locate leaks in the final cover for landfills or impoundments. The method will not damage the liner.

TECHNICAL DISCUSSION

METHOD

Figure 1 shows the basic electrical leak location method for detecting and locating leaks in a geomembrane liner. The leak location method makes use of the high electrical resistivity of the geomembrane liner material. When no leaks are present, a voltage impressed across the liner produces a relatively uniform voltage potential distribution in the material above the liner. If the liner is punctured or separated physically, conductive fluid flows through the leak establishing a conductive path for current flow, which produces an anomaly in the measured potential in the vicinity of the leak.

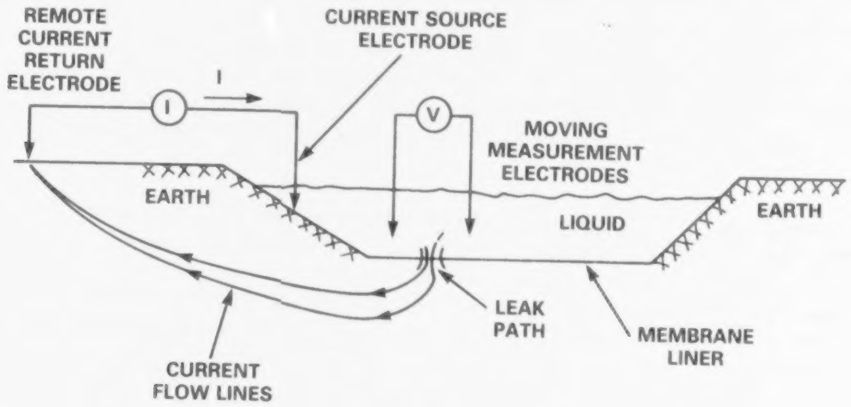


Figure 1. Diagram of the electrical leak location method.

Therefore, leaks can be located by measuring the potential distribution patterns in the material covering the liner.

COMPUTER SIMULATION MODEL

A computer model was developed to investigate the performance capabilities of the electrical leak location method. The model can accommodate various electrical and dimensional parameters in the three layers comprising the lined impoundment or landfill. The electrical anomaly of a circular hole in a thin, highly resistive layer was used to model the response of a geomembrane lined impoundment or landfill containing a damaged geomembrane liner. The secondary potential for a leak in a geomembrane liner is in the form of an integral equation, which includes a three-layer medium Green's function.* The excellent agreement between experimental and synthetic model data verified the accuracy of the general solution for predicting leak signatures.

Model studies of the electrical leak detection survey technique were made to characterize the performance of the method under various conditions of the electrical parameters of the waste materials, the measurement electrode array, the measurement dipole depth and proximity to the leak, the size and number of leaks, and the impoundment depth. Figure 2 shows a typical

Key:

s = electrode spacing
h = depth of the water
ρ_w = liquid resistivity
ρ_s = underlying soil resistivity
a = leak radius
z_m = electrode depth
x = offset distance

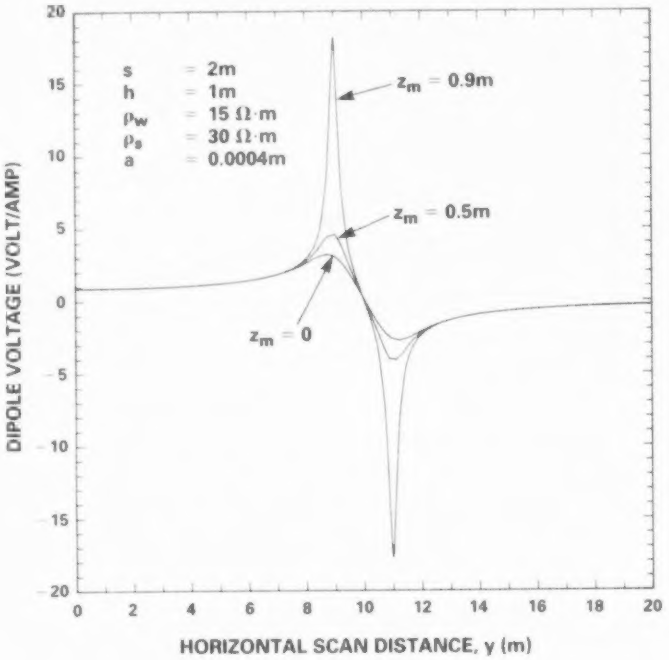


Figure 2. Plot of the leak anomaly versus electrode depth.

---

*A Green's function is the solution to the Laplace's equation with a unit current source. The specific Green's function for this solution is found in Darilek and Parra, March 1988, The Electrical Leak Location Method for Geomembrane Liners: Final Technical Report, EPA Contract No. CR-811771-01-3.

family of leak anomaly responses illustrating the effects of various measurement depths for a single leak located in a liquid waste impoundment. A substantial improvement in detection sensitivity is obtained when the potential array is closer to the leak. The peak-to-peak anomaly amplitudes for different waste layer resistivity values were calculated. When a constant current is injected, the leak detectability is increased linearly with the resistivity of the waste material.

Figure 3 shows the peak-to-peak anomaly responses calculated for various dipole offset distances from the leak center as a function of the survey height above the liner. An improvement in leak detectability is observed for survey lines located within a radius of 10 cm from the leak center when the depth of the detector is increased.

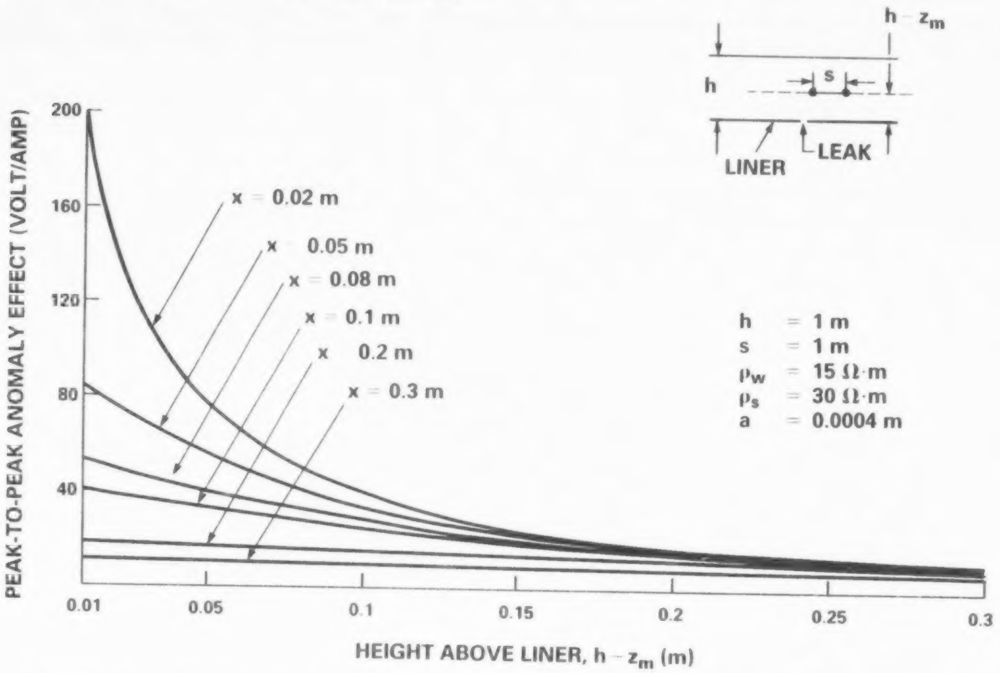


Figure 3. Peak-to-peak voltage anomaly versus electrode scan offset distance.

Figure 4 shows that the horizontal dipole response is stronger than the vertical dipole response. Figure 5 shows a typical vertical dipole anomaly response of a leak. The leak is directly associated with the maximum anomaly response. For practical reasons, leaks may be located more easily and accurately with a vertical dipole because the leak is located at the peak of the unipolar response rather than the bipolar anomaly with the horizontal dipole. Multiple leaks can be resolved with less ambiguity when a vertical dipole is used.

Leak signatures for various multiple leak geometries were computed. Figure 6 shows horizontal dipole leak signatures computed for two survey

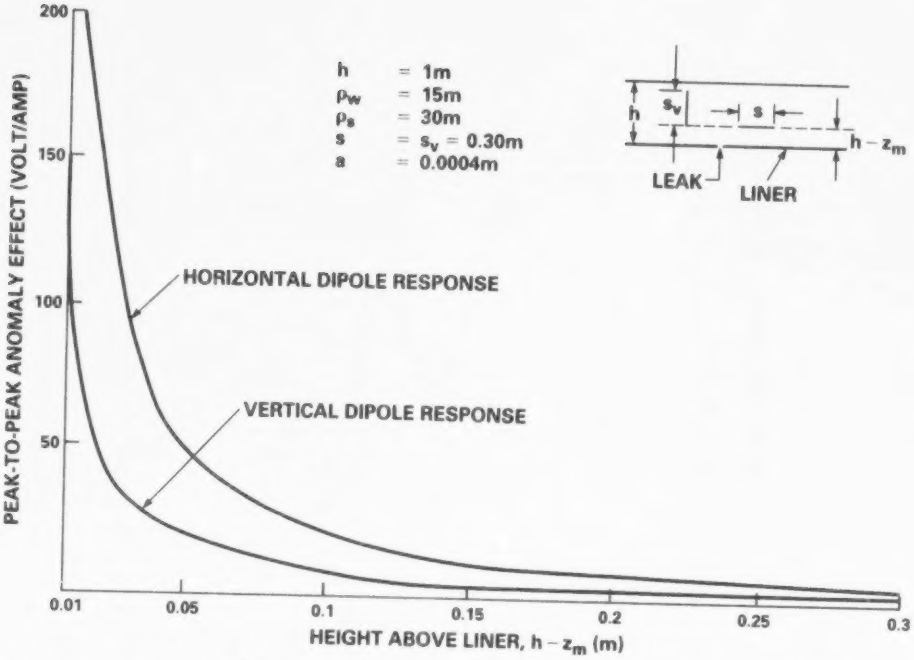


Figure 4. Comparison of leak anomaly amplitudes for horizontal and vertical measurement dipoles.

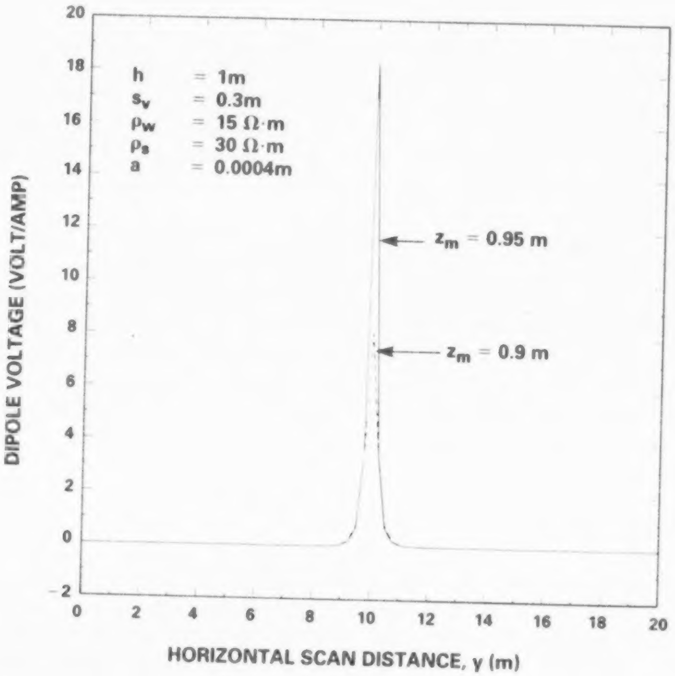


Figure 5. Leak anomaly characteristic of a vertical dipole.

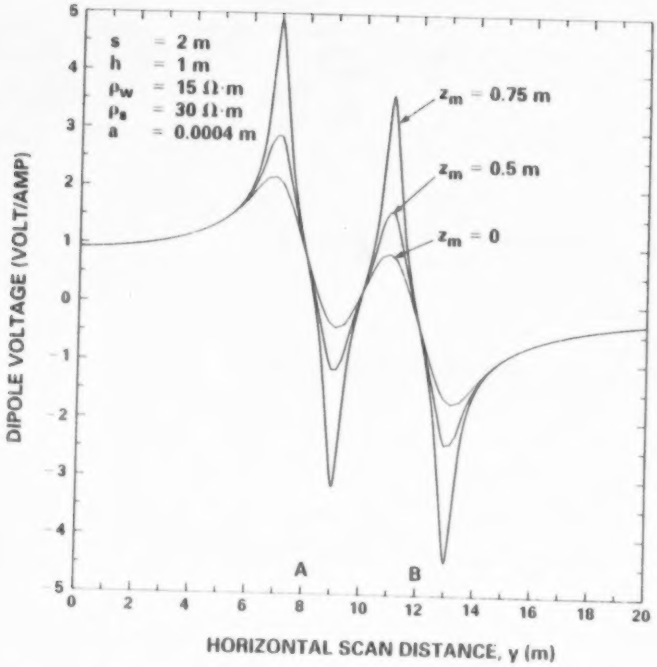


Figure 6. Leak anomaly for multiple leaks.

depths when the leaks are spaced two meters apart. As expected, when the horizontal separation between leaks becomes less than the horizontal dipole spacing, separate resolution of the two leaks is lost. When leaks are located at separations approximating the horizontal dipole detector spacing, the resolution is poor. However, when measurements are acquired using a small dipole detector spacing, the resolution is improved.

The derived geomembrane leak detection model can be used to aid in planning surveys and processing leak survey data acquired in lined impoundments or landfills. The computed leak responses point out the practical importance of performing the survey measurements near the bottom of the impoundment. The results also indicate that the horizontal dipole detector spacing must be less than the leak separation or a vertical dipole must be used to improve leak resolution. The injected current must be increased to offset the effect of lower measured leak anomaly attributed to lower resistivity of the liquid.

DOUBLE LINER MODEL TESTS

By placing the current return electrode in electrical contact with the liquid-saturated drainage layer located between the two liners, the electrical leak location method is applicable for detecting and locating leaks in the upper liner. Simple electrical continuity tests between the drainage layer and the earth can determine the existence of leaks in the bottom liner, but not the location of that leak.

A scale model with dimensions of 3 m × 3 m was used to test the electrical leak location method for locating leaks with various impoundment configurations, including different types of drainage layers, various types of leaks, and a protective soil cover over the primary liner. Figure 7 is a contour plot of the data for a leak with a diameter of 5.1 mm with a drainage layer consisting of a sandy loam soil layer placed over geotextile mat, which is then placed over the geonet material. The location of the leak is clearly indicated by the dipolar contour pattern. The potential gradient pattern caused by the current injection electrode is also evident in the data. Other tests indicated that a leak with a diameter of 25 mm and a 15-cm slit leak produce anomaly characteristics very similar to the leak with a diameter of 5.1 mm. However, the larger leaks required less voltage to produce the same anomaly amplitude.

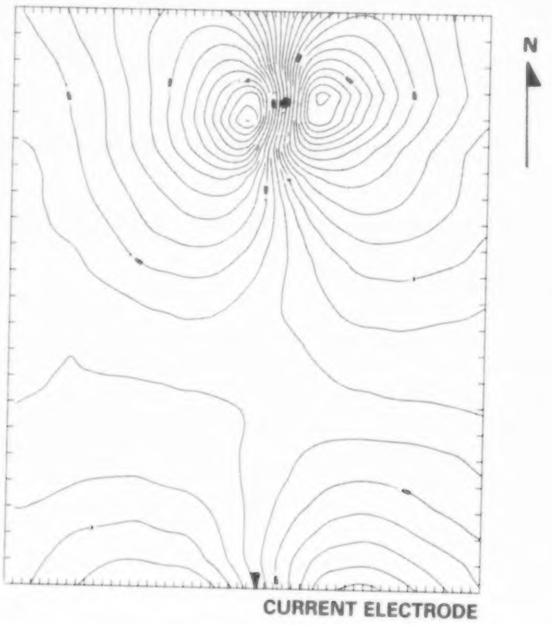


Figure 7. Contour plot of double liner model data.

Tests were conducted using various electrode materials and geometries to determine the best and most practical electrode configurations for electrical leak location surveys in liquid-filled impoundments. Figure 8 shows the relative leak anomaly amplitudes for various electrodes when the centerlines of the electrodes were scanned directly over the leak, and 15 cm offset from the leak. When the electrodes were scanned directly over the leak, the anomaly amplitudes were inversely related to the length of the electrodes. However, when the electrodes were scanned along a line 15 cm from the leak, the 30-cm line electrode produced the largest anomaly. More importantly, the leak anomaly was barely detected when the localized point electrodes passed within 15 cm of the leak, where the longer electrodes produced easily detectable anomalies.

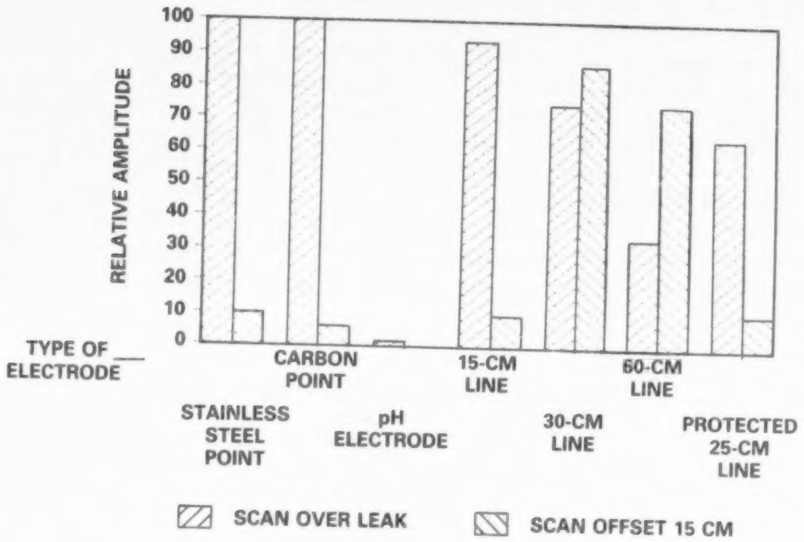


Figure 8. Relative anomaly amplitudes for various measurement electrodes.

LOCATING LEAKS IN COVER SYSTEMS

The electrical leak location method was adapted to make surface soil potential measurements to locate leaks in final cover system geomembrane liners. Half-cell electrodes were used to reduce the polarization noise caused by electrochemical reactions at the interface between the soil and metal electrodes. These electrodes typically consist of a plastic tube with a porous ceramic tip. Electrical contact is made through a metal electrode in a saturated salt solution in the half-cell.

Experiments were conducted using a physical model with dimensions of 5 m × 5 m. Figure 9 is a plot of the measured leak anomaly for several soil cover thicknesses. Although the peak-to-peak amplitude of the anomaly decreases rapidly with increasing soil cover, the leak was easily detected for all of the soil cover depths tested. Tests were performed with 60 cm of soil cover to show that electrode contact noise is reduced significantly when the electrodes are inserted in the ground to a depth of approximately 25 mm or when the dry ground surface is scraped off prior to the measurements.

Other methods for detecting leaks in the geomembrane liner of cover systems, including ground-penetrating radar, tracer gas, the electromagnetic induction method, encapsulated chemicals, and electronic transponders, were analyzed. The most promising method studied for locating leaks in final cover systems, other than the electrical leak location method, is ground-penetrating radar. Limited testing using infrared imaging was unsuccessful in detecting localized areas of low thermal conductivity caused by drainage of soil moisture through a leak.

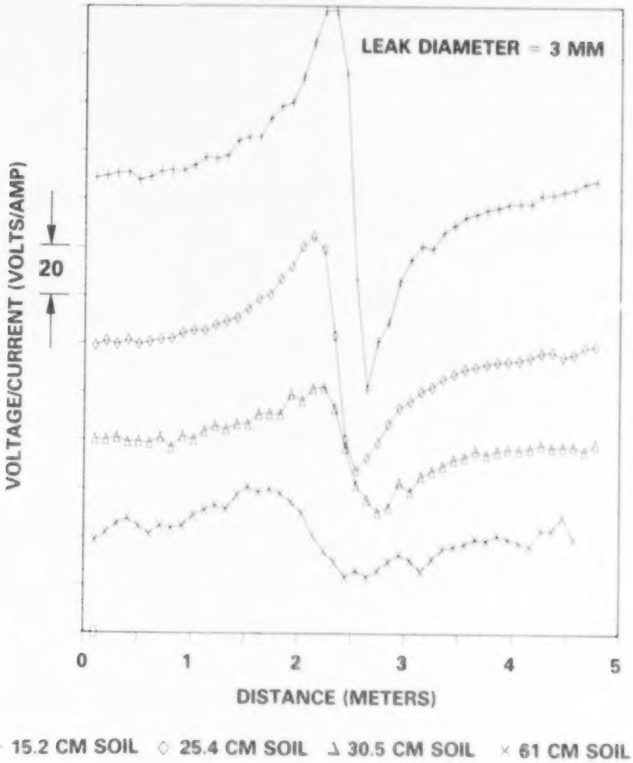


Figure 9. Measured leak anomaly for various soil cover thicknesses.

LINER RESISTIVITY TESTS

Tests were conducted to measure electrical resistance changes in liners over a period of time to determine whether the electrical resistance of the liner materials changes after exposure to waste liquids, thereby reducing the usefulness of the survey technique. The tests were performed in triplicate using polyvinyl chloride, high-density polyethylene, two thicknesses of chlorosulfonated polyethylene, and chlorinated polyethylene. The liquids used in the tests included sodium hydroxide solution, pH of 10; sulfuric acid solution, pH of 1; sodium chloride solution, 10 percent by weight; and deionized water.

The laboratory tests indicated that there was no significant decrease in the resistivity of the liner materials during a 13-week exposure. Exposure of these typical liner materials to these chemicals had no effect on the applicability of the electrical leak location method.

FIELD DEMONSTRATION SURVEYS

Full-scale surveys at the Southwest Research Institute test impoundment were performed to detect and locate four small circular leaks, each 0.79 mm in diameter. The impoundment was filled with water to a depth of approximately 46 cm and the measurement electrodes were immersed at a depth of 30 cm. The contour plot of the data shown in Figure 10 graphically indicates the locations of the four leaks.

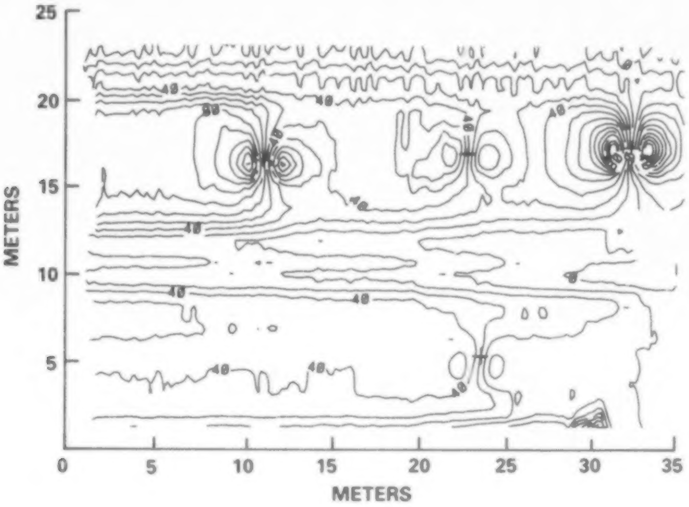


Figure 10. Contour plot of data at a full-scale impoundment.

The electrical leak location method was demonstrated at another full-scale impoundment in the San Antonio, Texas area. Although the complete liner had been tested previously using the vacuum box method, a 2.0-cm long leak was found. The characteristic leak anomaly was clearly evident on scan lines as far away from the leak as 1.5 m, and no false indications were obtained.

CONCLUSIONS

An electrical method for detecting and locating leaks in geomembrane liners for hazardous waste impoundments and landfills has been developed and demonstrated successfully in a wide variety of applications. The project demonstrates the validity and usefulness of the electrical leak location method for testing the integrity of the geomembrane for single and double liners and final cover systems. The technique is cost effective for construction quality assurance and in-service performance monitoring. Additional development will bring the method into application for hazardous material impoundments and for final cover systems.

SUPERFUND STANDARD ANALYTICAL REFERENCE MATRIX PREPARATION AND RESULTS OF PHYSICAL SOILS WASHING EXPERIMENTS

by: M. Pat Esposito*, Barbara Bruce Locke, and Jack Greber
PEI Associates, Inc.
Cincinnati, Ohio 45246
and
Richard P. Traver
U.S. EPA, HWERL

ABSTRACT

In response to the RCRA Hazardous and Solid Waste Amendments of 1984 prohibiting the continued land disposal of untreated hazardous wastes, the EPA has instituted a research program for establishing best demonstrated and available technologies for RCRA and Superfund wastes. Under Phase I of EPA's Superfund research program, several projects were initiated under which a surrogate soil containing a wide range of chemical contaminants was prepared for use in bench-scale and pilot-scale performance evaluations of five different treatment technologies. This paper covers one of the projects in which the surrogate test soil was developed and bench-scale soil washing treatability studies were completed. This work was conducted by PEI Associates under EPA Contract No. 68-03-3413 during 1987. This paper has been reviewed in accordance with the U.S. Environmental Protection Agency's peer and administrative review policies and approved for presentation and publication.

---

* Formerly with PEI, now with Bruck, Hartman & Esposito, Inc., Cincinnati, Ohio.

INTRODUCTION

The RCRA Hazardous and Solid Waste Amendments of 1984 prohibit the continued land disposal of untreated hazardous wastes beyond specified dates. The statute requires the U.S. Environmental Protection Agency (EPA) to set "levels or methods of treatment, if any, which substantially diminish the toxicity of the waste or substantially reduce the likelihood of migration of hazardous constituents from the waste so that short-term and long-term threats to human health and the environment are minimized." The legislation sets forth a series of deadlines beyond which further disposal of particular waste types is prohibited if the Agency has not set treatment standards under Section 3004(m) or determined, based on a case-specific petition, that no further migration of hazardous constituents will occur for as long as the wastes remain hazardous.

In addition to addressing future land disposal of specific listed wastes, the RCRA land disposal restrictions also address the disposal of soil and debris from CERCLA site response actions. Sections 3004(d)(3) and (e)(3) of RCRA state that the soil/debris waste material resulting from a Superfund-financed response action or an enforcement authority response action implemented under Sections 104 and 106 of CERCLA, respectively, will not be subject to the land ban until November 8, 1988.

Because Superfund soil/debris waste often differs significantly from other types of hazardous waste, the EPA is developing specific RCRA Section 3004(m) standards or levels applying to the treatment of these wastes. These standards will be developed through the evaluation of best demonstrated and available technologies (BDAT). In the future, Superfund wastes in compliance with these regulations may be deposited in land disposal units; wastes exceeding these levels will be banned from land disposal unless a variance is issued.

In early 1987, EPA's Hazardous Waste Engineering Research Laboratory, at the request of the Office of Solid Waste, initiated a research program to evaluate various treatment technologies for contaminated soil and debris from Superfund sites. Under Phase I of this research program, which was conducted from April to November 1987, a surrogate soil containing a wide range of chemical contaminants typically occurring at Superfund sites was prepared for use across the board in the bench-scale or pilot-scale performance evaluations of five available treatment technologies: 1) soil washing, 2) chemical treatment (KPEG), 3) thermal desorption, 4) incineration, and 5) stabilization/fixation. This report covers those segments of Phase I related to development of the surrogate soil and experimental bench-scale tests on the potential effectiveness of physical soil washing as a treatment technology.

PROCEDURES

SARM PREPARATION

The surrogate soil is referred to throughout the text as SARM, an acronym for Synthetic Analytical Reference Matrix. More than 30,000 pounds of clean (uncontaminated) SARM was prepared after considerable research into the types of soils found at Superfund sites nationwide. The final composition selected consisted of 30 percent by volume clay (a mixture of montmorillinite and kaolinite), 25 percent silt, 20 percent sand, 20 percent topsoil, and 5 percent gravel. The components were air-dried to minimize moisture and then mixed together in two 15,000-lb batches in a standard truck-mounted 6-yd^3 cement/concrete mixer.

A prescribed list of chemicals found to be widely and frequently occurring at Superfund sites was then added to the clean SARM in a series of smaller-scale mixing operations utilizing a 15-ft^3 mortar mixer. The organic chemicals added included ethyl benzene, 1,2-dichloroethane, tetrachloroethylene, acetone, chlorobenzene, styrene, xylene, anthracene, pentachlorophenol, and bis(2-ethylhexyl) phthalate. Salts or oxides of the following metals were also added: lead, zinc, cadmium, arsenic, copper, chromium, and nickel. Because concentrations of contaminants in soils vary widely, four different SARM formulas containing either high or low levels of organics and metals were prepared for use in subsequent treatability tests using the five technologies named. Table 1 presents the target contaminant concentration of the four SARMs prepared. Reserves of each SARM were also packaged and archived for future use. The archived samples are being stored at EPA's R&D facility in Edison, New Jersey.

PHYSICAL SOIL WASHING EXPERIMENTS

As part of the performance evaluation of soil washing as a potential treatment candidate, samples of each SARM were physically washed in a series of bench-scale experiments designed to simulate the EPA-developed Mobile Soils Washing System (MSWS). This system can extract certain contaminants from soils, which reduces the volume of the contaminated portion of the soils. The MSWS is expected to be an economic alternative to the current practice of hauling contaminated soils offsite to a landfill and replacing the excavated volume with fresh soils.

Specifically, this project was designed to simulate the drum screen washer segment of the MSWS as described by J.S. Shum in the Operation and Maintenance Manual(1). This segment of the MSWS separates the +2 mm soil fraction from the -2 mm soil fraction (fines) by use of a rotary drum screen. A high-pressure water knife operates at the head of the system to break up soil lumps and strip the contaminants off the soil particles. Both the design of the MSWS and the design of the bench-scale experiments to simulate the MSWS for cleanup of the SARMS samples are based on the following assumptions, which underlie the volume reduction approach of physical soils washing:

1. A significant fraction of the contaminants are attached to the silt, humus, and clay particles.

2. The silt and clay are attached to the sand and gravel by physical processes (primarily compaction/adhesion).

3. Physical washing of the sand/gravel/rock fraction will effectively remove the fine sand, silt, and clay-sized (less than 0.25 mm) materials from the coarse material.

TABLE 1. TARGET CONTAMINANT CONCENTRATIONS FOR SARMS
(mg/kg)

Analyte	SARM I (High organic, low metal)	SARM II (Low organic, low metal)	SARM III (Low organic, high metal)	SARM IV (High organic, high metal)
Volatiles				
Acetone	6,800	680	680	6,800
Chlorobenzene	400	40	40	400
1,2-Dichloroethane	600	60	60	600
Ethylbenzene	3,200	320	320	3,200
Styrene	1,000	100	100	1,000
Tetrachloroethylene	600	60	60	600
Xylene	8,200	820	820	8,200
Semivolatiles				
Anthracene	6,500	650	650	6,500
Bis(2-ethylhexyl) phthalate	2,500	250	250	2,500
Pentachlorophenol	1,000	100	100	1,000
Inorganics				
Arsenic	10	10	500	500
Cadmium	20	20	1,000	1,000
Chromium	30	30	1,500	1,500
Copper	190	190	9,500	9,500
Lead	280	280	14,000	14,000
Nickel	20	20	1,000	1,000
Zinc	450	450	22,500	22,500

4. The contaminants will be removed to the same extent that the silt and clay are separated (i.e., increasing the efficiency of the washing process will directly increase the removal efficiency for the majority of the contaminant mix).

These assumptions were tested by evaluating different wash solutions in bench-scale shaker-table experiments. The wash solutions chosen for evaluation included 1) a chelant solution (tetrasodium salt of EDTA, Dow Chemical Versene 100^{R}), and 2) an anionic surfactant solution (phosphated formulation from Procter and Gamble, Institutional Formula Tide^{R}). Different pH and temperature conditions were evaluated for the wash solutions. Organic solvents and oxidizing agents were considered, but were found not to be viable soil-washing solutions because of material handling problems associated with these compounds, especially when used in a field situation. Following the shaker-table wash, the soil was wet-sieved to separate the fines from the coarse material. Although the EPA MSWS only separates the soil into +2 mm and -2 mm size fractions, three size fractions (+2 mm, 250 µm to 2 mm, and -250 µm) were investigated in this study to determine if an intermediate size fraction (medium to fine sand) could be cleaned effectively, thereby increasing the volume reduction potential. For determination of the effectiveness of the soil-washing techniques in reducing the volume of contaminated material, each of the resulting soil fractions was subsequently analyzed for total organics and metals by standard Gas Chromatography Mass Spectrometry (GC/MS) and Inductively Coupled Plasma (ICP) techniques (SW-846, 3rd ed.) and for leachable constituents by Toxicity Characteristic Leaching Procedures (TCLP).

RESULTS

SARM PREPARATION

Results of physical tests conducted on the clean SARM are summarized in Table 2. These test results indicate that the synthetic soil is characteristic of a slightly alkaline sandy loam with moderate clay and organic content and a relatively high cation exchange capacity. Such a soil, when contaminated, should present a reasonable challenge to any applied treatment technology.

Chemical analyses of samples of the four SARMs were conducted before treatment to verify contaminant levels and moisture content. Table 3 contains the average concentrations obtained for each analyte in each of the four SARMs. All numbers reported by each laboratory conducting the analyses (five separate analytical laboratories performed these analyses) were included in calculating the averages.

If the target contaminant levels (Table 1) are compared to the actual levels found (Table 3), the recovery efficiencies obtained are the highest and most consistent for the metals, followed by the volatiles and the semivolatiles. Generally, the SARMs containing the higher concentrations of volatiles and semivolatiles showed better corelation between the target and the actual contaminant levels. The results for the lower organic contaminated SARMs (SARM II and III) seem to indicate either that a greater portion (relative to the high organic SARMs) of the indicator organics added to the soil were lost through one or more routes (e.g., volatilization, adsorption), or alternatively, that the lower concentrations of the organics were more difficult to reliably detect and quantitate.

TABLE 2. PHYSICAL CHARACTERISTICS OF CLEAN SARM

	Average[a]	Range
Cation exchange capacity, meq/100 g	132.7 (10)	77.5 to 155
Total organic carbon, %	3.2 (6)	2.7 to 3.9
pH	8.5 (6)	8.0 to 9.0
Grain size distribution, weight %		
Gravel (>4.75 mm)	3 (6)	2 to 4
Sand (4.75 mm - 0.075 mm)	56 (6)	54 to 58
Silt (0.074 mm to 0.005 mm)	28 (6)	27 to 30
Clay (<0.005 mm)	12 (6)	11 to 14

[a] Values in parentheses indicate number of samples analyzed.

TABLE 3. ANALYTICAL PROFILE OF SARMS: AVERAGE CONCENTRATION FOUND UPON ANALYSIS[a] (mg/kg)

Analyte	SARM I	SARM II	SARM III	SARM IV
	(High organic, low metal)	(Low organic, low metal)	(Low organic, high metal)	(High organic, high metal)
Volatiles				
Acetone	4,353 (9)	356 (8)	358 (2)	8,030 (2)
Chlorobenzene	316 (9)	13 (6)	11 (2)	330 (2)
1,2-Dichloroethane	354 (9)	7 (8)	5 (2)	490 (2)
Ethylbenzene	3,329 (9)	123 (8)	144 (2)	2,708 (2)
Styrene	707 (9)	42 (8)	32 (2)	630 (2)
Tetrachloroethylene	408 (9)	19 (8)	20 (2)	902 (2)
Xylene	5,555 (9)	210 (8)	325 (2)	5,576 (2)
Semivolatiles				
Anthracene	5,361 (9)	353 (7)	181 (3)	1,920 (3)
Bis(2-ethylhexyl) phthalate	1,958 (9)	117 (7)	114 (3)	646 (3)
Pentachlorophenol	254 (9)	22 (7)	30 (3)	80 (3)
Metals				
Arsenic	18 (10)	17 (7)	652 (4)	500 (4)
Cadmium	22 (8)	29 (6)	2,260 (2)	3,631 (2)
Chromium	24 (8)	28 (6)	1,207 (4)	1,314 (4)
Copper	231 (10)	257 (8)	9,082 (4)	10,503 (4)
Lead	236 (10)	303 (8)	14,318 (4)	14,748 (4)
Nickel	32 (10)	38 (8)	1,489 (4)	1,479 (4)
Zinc	484 (8)	642 (6)	31,871 (4)	27,060 (4)
Moisture, %	20 (7)	11 (7)	19 (3)	26 (2)

---

[a] Values in parentheses indicate number of samples analyzed.

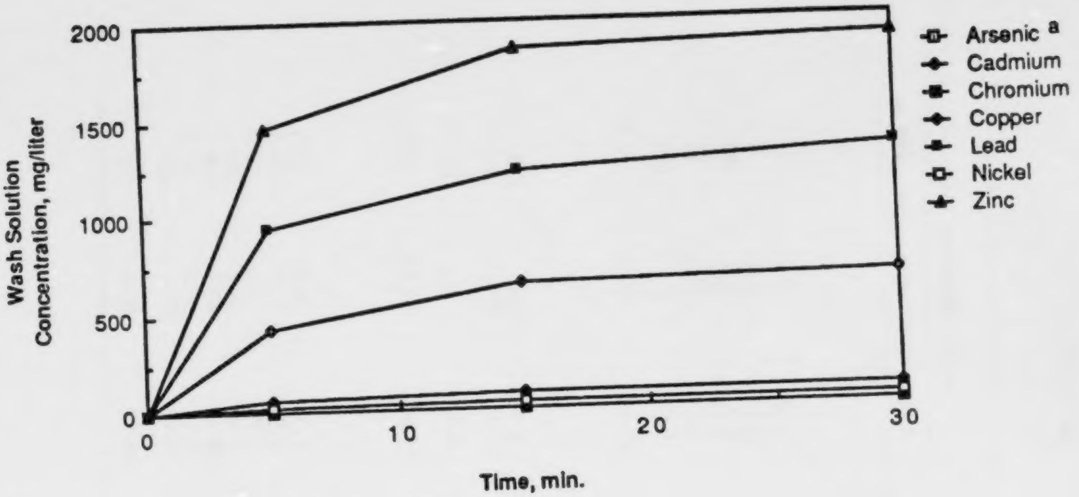
PHYSICAL SOIL WASHING EXPERIMENTS

During the initial phase of these experiments, pH and temperature variations were evaluated as well as different chelant and surfactant concentrations. Experiments were also run to determine the optimum reaction time for both the chelant and surfactant solutions. In all cases, a 10:1 wash solution-to-soil ratio was utilized. Temperature ranges from 78° to 120°F were found to have little effect on the contaminant reduction efficiencies. Adjustment of the pH of the surfactant solution from 5.0 to 12.0 resulted in no appreciable change in the organic contaminant removal efficiencies. Also, reducing the pH of the chelant solution from its natural pH of 12 to 8.0 produced no additional metal removal.

Reaction times of 5, 15 and 30 minutes were evaluated in a series of trial tests for the chelant and surfactant solutions in order to select the optimum reaction time for all subsequent testing. Figures 1 and 2 present the reaction time results for a 1:1 molar ratio (moles of tetrasodium EDTA to moles of total metals present in the SARM) chelant wash of metals from SARM III, and for a 0.1 percent (by weight) surfactant wash of organics from SARM I, respectively. The concentrations used for evaluation of the reaction times were the lowest concentrations of both chelant and surfactant chosen for overall evaluation in this study. As shown in Figure 1, no significant additional metal chelation occurred for SARM III after 15 minutes for any of the six metals. Therefore, a 15-minute reaction time was chosen for all of the subsequent chelant wash tests. As shown in Figure 2, no similar completion of reaction was evident for the organic contaminants (as total organic halogens); their concentration in the wash water continued to increase over the entire 30-minute interval. Therefore, 30 minutes was chosen as the reaction time for all subsequent surfactant washes. Longer reaction times were not evaluated because reaction times in excess of 30 minutes are typically too costly in scale-up operations.

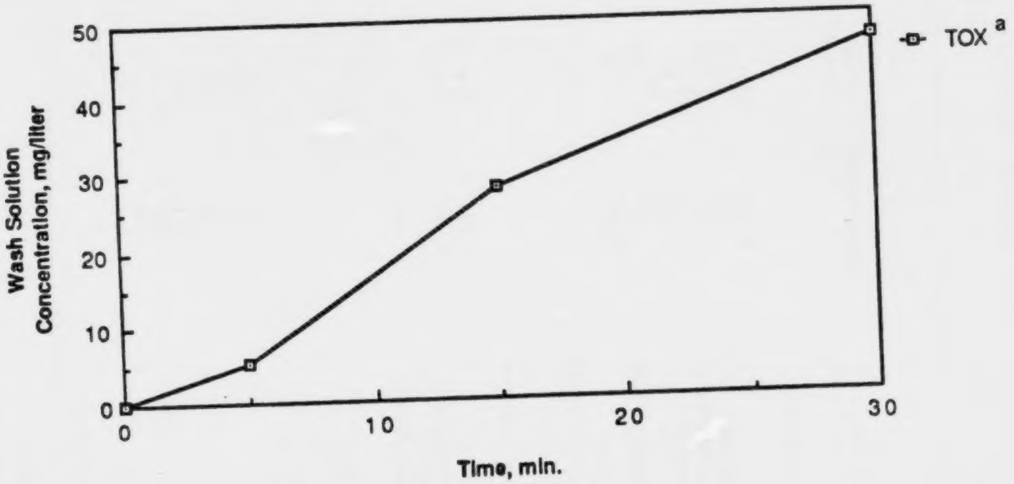
Next, surfactant concentrations of 1.5, 0.5, and 0.1 percent (by weight) were evaluated in a series of 30-minute washing tests of SARM I to determine the optimum organic contaminant removal efficiency achievable. The tests showed that the 0.1 percent solution was least effective, and that the 1.5 percent and 0.5 percent concentrations were essentially equal; the results obtained for the 1.5 percent solution did not indicate sufficient additional contaminant reduction over the 0.5 percent solution to justify the higher surfactant concentration. Thus the 0.5 percent surfactant solution was chosen as the optimum wash concentration for subsequent organics removal tests. Two molar ratios (moles of tetrasodium EDTA to total moles of metals present in the higher metal SARM-SARM III) were evaluated for metals removal--1:1 and 3:1. The 3:1 EDTA molar ratio solution exhibited consistently higher removal efficiencies for the metals, particularly in the middle soil fraction (250 μm to 2 mm); therefore it was chosen for further study in all subsequent metal removal tests.

During the second phase of these experiments, the optimum conditions for reducing organic and metal contamination (as determined in the initial phase of the soil experiments and discussed in the preceding paragraphs) were applied to all four SARMs and compared with a baseline plain water wash for each SARM. Tables 4 through 7 present the results of these final washings. In



[a] Arsenic and nickel overlap in this figure.

Figure 1. Reaction time - 1:1 molar chelant wash, SARM III



[a] Total organic halogens

Figure 2. Reaction time - 0.1% surfactant wash, SARM I

TABLE 4. SOIL WASHING RESULTS: SARM I (HIGH ORGANICS, LOW METALS) (ppm)

Contaminant	Initial concentration[a]	Water wash >2 mm	Water wash 250 µm to 2 mm	Water wash <250 µm	0.5% Surfactant wash >2 mm	0.5% Surfactant wash 250 µm to 2 mm	0.5% Surfactant wash <250 µm
Volatile organics							
Acetone	4,353	10	20	140	22	8.0	50
Chlorobenzene	316	0.028	0.28	160	0.30	1.0	31
1,2-Dichloroethane	354	<0.023	0.18	24	0.15	0.32	6.0
Ethyl benzene	3,329	0.13	1.4	2300	2.3	8.5	680
Styrene	707	ND[b]	ND	400	<0.17	ND	96
Tetrachloroethylene	408	0.009	0.12	250	0.20	0.81	49
Xylene	5,555	0.38	3.2	1800	4.0	14	820
Total volatile organic reduction		>99.9%	99.8%	66.2%	>99.8%	99.8%	88.5%
Semivolatile organics							
Anthracene	5,361	6.5	3200	1400	3.3	2500	2700
Bis(2-ethylhexyl) phthalate	1,958	4.0	92	1600	<6.1	100	1600
Pentachlorophenol	254	66	26	53	8.4	4.6	ND
Total semivolatile organic reduction		98.9%	56.2%	59.7%	>99.8%	65.6%	43.2%
Inorganics							
Arsenic	18	3.0	5.2	18.6	4.5	5.8	19.1
Cadmium	22	7.3	11.3	28.8	6.9	11.0	26.2
Chromium	24	1.5	2.6	43.4	3.0	3.0	46.8
Copper	231	10.6	30.5	387	11.8	34.6	384
Lead	236	11.1	28.8	402	10.1	40.1	420
Nickel	32	3.2	7.8	35.1	5.1	6.8	31.6
Zinc	484	44.8	106	726	47.9	101	647
Total metal reduction		92.2	81.6	NR[c]	91.5	80.7	NR

[a] From Table 3.

[b] ND = not detected.

[c] NR = no reduciton in overall contamination.

TABLE 5. SOIL WASHING RESULTS: SARM II (LOW ORGANICS, LOW METALS)
(ppm)

Contaminant	Initial concentration[a]	Water wash			3:1 Molar chelant wash			0.5% Surfactant wash		
		>2 mm	250 µm to 2 mm	<250 µm	>2 mm	250 µm to 2 mm	<250 µm	>2 mm	250 µm to 2 mm	<250 µm
Volatile organics										
Acetone	356	0.50	0.31	0.50	0.58	1.2	2.7	0.46	0.75	1.8
Chlorobenzene	13	0.002	0.013	<0.23	<0.004	0.006	0.020	0.002	0.002	ND
1,2-Dichloroethane	7	ND[b]	<0.004	ND	ND	0.003	0.003	ND	0.004	ND
Ethyl benzene	123	0.014	0.082	0.14	0.005	0.058	0.13	0.009	0.015	0.62
Styrene	42	0.016	0.13	0.25	<0.006	0.066	0.12	0.010	<0.013	0.28
Tetrachloroethylene	19	ND	<0.004	<0.22	ND	<0.004	0.009	ND	ND	<0.30
Xylene	210	0.040	0.31	0.52	0.021	0.20	0.44	0.028	0.040	1.3
Total volatile organic reduction		99.9%	>99.9%	>99.8%	>99.9%	>99.8%	99.6%	99.9%	>99.9%	>99.4%
Semivolatile organics										
Anthracene	353	3.2	180	830	8.8	210	660	1.6	120	700
Bis(2-ethylhexyl) phthalate	117	27	46	370	40	44	260	28	32	160
Pentachlorophenol	22	ND	6.8	4.6	ND	5.1	ND	2.4	7.8	ND
Total semivolatile organic reduction		93.9%	52.7%	NR[c]	90.1%	47.3%	NR	93.5%	67.5%	NR
Inorganics										
Arsenic	17	2.5	4.2	24.8	3.9	4.4	12.6	3.0	3.6	27.8
Cadmium	29	6.0	10.2	55.6	2.0	4.0	7.5	4.8	9.4	37.7
Chromium	28	<0.88	4.0	90.4	1.6	3.4	69.7	2.7	3.5	56.6
Copper	257	5.0	25.4	652	8.2	15.6	238	9.0	28.6	478
Lead	303	4.0	69.0	710	6.2	12.6	110	8.5	31.8	511
Nickel	38	4.0	7.2	68.6	4.2	7.0	43.0	3.2	6.8	41.8
Zinc	642	21.0	107	1380	28.3	63.6	546	25.8	112	906
Total metal reduction		>96.7%	82.7%	NR	95.9%	91.6%	21.9%	95.7%	85.1%	NR

[a] From Table 3.

[b] ND = not detected.

[c] NR = no reduction in overall contamination.

TABLE 6. SOIL WASHING RESULTS: SARM III (HIGH ORGANICS, LOW METALS)
(ppm)

Contaminant	Initial concentration[a]	Water wash			3:1 Molar chelant wash		
		>2 mm	250 μm to 2 mm	<250 μm	>2 mm	250 μm to 2 mm	<250 μm
Volatile organics							
Acetone	358	0.74	1.7	16	0.96	2.6	3.3
Chlorobenzene	11	0.008	0.16	1.6	0.011	0.23	1.2
1,2-Dichloroethane	5	<0.004	0.024	0.084	0.002	0.034	<0.050
Ethyl benzene	144	0.040	1.3	34	0.054	2.0	20
Styrene	32	0.026	<0.30	6.4	ND[b]	0.55	3.0
Tetrachloroethylene	20	0.002	0.16	3.0	0.006	0.23	2.2
Xylene	325	0.10	2.6	58	0.091	3.6	31
Total volatile organic reduction		>99.9%	>99.3%	86.7%	99.9%	99.0%	>93.2%
Semivolatile organics							
Anthracene	181	<5.6	480	1,800	1.7	540	1,800
Bis(2-ethylhexyl) phthalate	114	2.2	7.4	1,100	3.4	9.4	790
Pentachlorophenol	30	9.2	40	59	<6.6	13	<96
Total semivolatile organic reduction		>94.8%	NR[c]	NR	96.4%	NR	NR
Inorganics							
Arsenic	652	54.6	102	1,160	36.6	51.0	243
Cadmium	2,260	372	276	746	290	116	110
Chromium	1,207	3.8	14.8	2,590	3.2	9.2	1940
Copper	9,082	68.4	264	20,800	38.6	104	2250
Lead	14,318	122	491	30,600	98.1	171	1470
Nickel	1,489	18.6	42.2	1,570	17.5	28.2	472
Zinc	31,871	558	1010	48,200	500	519	6760
Total metal reduction		98.0%	96.4%	NR	98.4%	98.4%	78.2%

[a] From Table 3.

[b] ND = not detected.

[c] NR = no reduction in overall contamination.

TABLE 7. SOIL WASHING RESULTS: SARM IV (HIGH ORGANICS, HIGH METALS) (ppm)

Contaminant	Initial concentration[a]	Water wash >2 mm	Water wash 250 µm to 2 mm	Water wash <250 µm	3:1 Molar chelant wash >2 mm	3:1 Molar chelant wash 250 µm to 2 mm	3:1 Molar chelant wash <250 µm	0.5% Surfactant wash >2 mm	0.5% Surfactant wash 250 µm to 2 mm	0.5% Surfactant wash <250 µm
Volatile organics										
Acetone	8,030	5.8	5.8	120	16	21	180	14	15	53
Chlorobenzene	328	0.020	1.5	68	0.012	1.4	99	0.076	0.94	22
1,2-Dichloroethane	490	0.028	<0.34	<8.6	<0.004	<0.54	40	0.10	<0.30	4.4
Ethyl benzene	2,708	0.080	15	2,000	0.051	12	1000	0.52	7.4	300
Styrene	630	ND[b]	<2.8	150	<0.026	ND	200	0.17	ND	54
Tetrachloroethylene	902	<0.017	2.3	120	0.006	1.4	170	0.048	1.1	45
Xylene	5,576	0.18	25	3,200	0.11	23	1700	0.86	26	460
Total volatile organic reduction		>99.9%	>99.7%	>69.6%	>99.9%	>99.7%	81.8%	99.9%	>99.7%	95.0%
Semivolatile organics										
Anthracene	1,920	28	2700	5,200	40	1700	3300	2.4	1800	5,800
Bis(2-ethylhexyl) phthalate	646	5.8	34	3,100	9.6	70	2800	<5.6	26	1,500
Pentachlorophenol	80	23	39	360	8.4	22	<180	38	42	100
Total semivolatile organic reduction		97.8%	NR[c]	NR	97.8%	32.3%	NR	>98.3%	29.4%	NR
Inorganics										
Arsenic	500	126	110	924	63.4	91.7	180	30	110	538
Cadmium	3,631	348	286	643	279	210	107	308	336	739
Chromium	1,314	7.7	29.0	2,180	6.4	29.8	1480	5.9	32.5	1,500
Copper	10,503	148	467	18,400	80.6	332	1990	63.1	446	11,100
Lead	14,748	168	1260	23,900	103	272	1360	68.4	818	15,000
Nickel	1,479	29.8	56.4	1,240	19.4	70.7	284	14	62.9	618
Zinc	27,060	873	3320	36,200	558	4730	5160	462	3040	25,400
Total metal reduction		97.1%	90.7%	NR	98.1%	90.3%	82.2%	98.4%	91.8%	7.3%

[a] From Table 3.

[b] ND = not detected.

[c] NR = no reduction in overall contamination.

general, the cleaning results of the water wash, the 3:1 molar chelant wash, and 0.5 percent surfactant wash for the +2 mm soil fraction did not differ significantly. As hypothesized, the silt and clay particles appeared to be attached to the sand and gravel primarily by physical processes such as compaction and adhesion. These physical attractions are often related to the age of the soil and the contact time between the contaminants and soil particles. Because the SARM was a freshly prepared soil that had not been compacted, weathered, and aged, the physical forces of attraction are believed to have been relatively weak, a condition more typical of a spill site soil than an older soil found at an abandoned CERCLA site. Consequently, the water wash was as effective in cleaning the +2 mm soil fraction as the water-plus-additive solutions were.

Removal of contaminants from the medium-grained fraction (250 µm to 2 mm) appears to entail both physical and chemical processes. By nature, this middle soil fraction, which is composed of medium to fine sand, does not absorb contaminants to the degree that clays and silts do. It has more surface area, however, and should be somewhat harder to clean than the coarse +2 mm fraction. A comparison of the water wash with the 3:1 molar chelant wash showed that the chelant wash reduced the residual concentration of metals in the medium soil size class for each SARM subjected to the chelant wash (SARM II, III, and IV). This trend is especially apparent in the data for SARM II (Table 5) where the total residual metal reduction increased from 82.7 percent for the water wash to 91.6 percent after the chelant wash. The organics show less variation among experimental runs in this soil size class. For the most part, water was as effective as the surfactant wash for reducing the level of organic contamination. The one anomaly was anthracene, which showed very high concentrations in the medium soil class. The anthracene evidently was not fully dissolved before it was added to the SARM; flakes of what was believed to be anthracene were observed on the 250 µm screen during the washing experiments.

Reduction of contaminants appears to be affected more by the use of different wash solutions in the fine soil fraction (less than 250 µm) than in the other soil fractions. Contaminants are typically bound by both chemical and physical processes in fine soil fraction. As shown in Tables 5 through 7, the chelant wash significantly reduced metal contamination in the fine soil fraction. This reduction is particularly evident in Tables 6 and 7, which present the results for the SARMs initially high in metal content. Although the spent wash water was not analyzed, it can be assumed that the chelant effectively mobilized the metals into solution. Similarly, the surfactant wash significantly reduced the volatile organic contamination in the fine soil fraction, as evidenced by the results shown in Tables 4 and 7 for the high-organic-content SARMs. Again, the wash water was not analyzed; however, it can be assumed that the surfactant successfully mobilized the organics into solution.

The trends indicated by the results of the TCLP analysis were similar to those shown in Tables 4 through 7. In general, reduction efficiencies ranging from 93 to 99 percent were obtained in the TCLP analysis of volatile organics, semi-volatile organics, and metals for the top two soil fractions (+2 mm and 2 mm to 250 µm). Most of the TCLP contaminants present in the +2 mm soil fractions dropped below the proposed regulatory limit given in the Federal Register, Volume 51, No. 114, June 13, 1986. In the SARMs containing lower levels of metals (specifically SARM I and II), the middle soil fraction (2 mm to 250 µm) also exhibited concentrations below the proposed TCLP levels.

CONCLUSIONS AND RECOMMENDATIONS

SARM PREPARATION

The preparation of a standard synthetic surrogate soil with physical characteristics and contaminant levels representative of a wide range of conditions typically found at Superfund sites was successfully completed. The surrogate or SARM was subsequently utilized in evaluating the relative effectiveness of five selected treatment technologies (physical soil washing, chemical treatment, stabilization, low temperature thermal desorption, and incineration), and a soil treatability data base has now been established.

Further studies comparing the treatability results that were obtained with the SARM to results from similarly designed studies using actual site soils are needed to further supplement the data base. Also, future studies in which the SARM is used to evaluate the relative effectiveness of other proposed treatment technologies at Superfund sites would be valuable.

PHYSICAL SOIL WASHING EXPERIMENTS

The soil washing results from this study appear to support the basic assumptions underlying the volume-reduction approach to site remediation--that a significant fraction of the contaminants in contaminated soils are attached to the smaller sized particles or fines (i.e., silt, humus, and clay) and that the coarse material can be cleaned and returned to the site by physically washing and separating it form the fines. The data indicate that water alone can efficiently remove a significant portion of the contamination from the +2 mm soil fraction. Contaminant removal from the middle (2 mm to 250 µm) soil fraction and the fine (<250 µm) soil fraction, however, can be generally enhanced by chelant and surfactant solutions. Addition of a chelant to the wash solution can improve metal reduction efficiencies for both the medium and small particle size fractions. Addition of a surfactant to the wash solution can lead to higher organic removals (compared with the water wash) from the fine particles. In general, water appears to be more effective in mobilizing the organics into solution than in mobilizing the metals.

In the preliminary bench-scale experiments, it was determined that the SARM was approximately 13 percent (by weight) coarse material (i.e., >2 mm), 29 percent medium-grained material (250 µm to 2 mm), and 58 percent fines (<250 µm). Therefore, the data presented in Tables 4 through 7 indicate achievement of at least a 13 percent weight reduction of contaminated material with a water wash alone. Addition of a chelant solution resulted in a 42 percent reduction by weight of the metal-contaminated SARM, and use of the chelant and surfactant solutions resulted in lower metal and organic contamination, respectively, in the fine particles.

The mix of contaminants in Superfund soils often lends itself to an extraction or washing treatment technology such as that demonstrated in this study. Although promising results have already been achieved at the pilot scale at a number of lead-contaminated Superfund sites, additional research is needed to demonstrate the cost-effectiveness of soil washing for full-scale treatment of a wide range of metal- and organic-contaminated soils. Specifically, most of the research conducted to date has involved demonstration of the operation of various pieces of equipment for pretreatment and extraction of the contaminants from the soil and for post-treatment of the extractant. The effective separation of the wash solution from the soil, the recycling of the regenerated wash solution, and the concentration/destruction of the contaminants, however, have not been demonstrated at a large-scale pilot facility(2). The following is a listing of areas in which future work is needed with respect to the development of soil washing as a full-scale, viable treatment option for Superfund soils:

1. Laboratory feasibility studies for evaluating removal of contaminants from the wash water.

2. Laboratory-scale physical soil washing studies using actual Superfund soils containing a mix of metal and organic contamination. (The first study of this type is currently funded and should begin in the spring of 1988.)

3. Evaluation of sequential wash solutions for reducing combined organic and metal contamination.

4. Additional pilot-scale studies on the use of the EPA Mobile Soil Washing System.

5. Bench-scale feasibility studies evaluating stabilization/solidification effectiveness as a treatment train option for the concentrated fines remaining after soil washing.

6. Evaluation of feed stock preparation methods for the EPA Mobile Soil Washing System.

REFERENCES

1. Shum, J. S. Drum Screen Washer Operation and Maintenance Manual. Prepared for the U.S. Environmental Protection Agency, Hazardous Waste Engineering Research Laboratory, Releases Control Branch, by Mason & Hanger-Silas Mason Company, Inc., under Contract No. 68-03-3203. February 1987.

2. Dietz, D. H., et al. Cleaning Contaminated Excavated Soil Using Extraction Agents (Draft). Prepared for the U.S. Environmental Protection Agency, Hazardous Waste Engineering Research Laboratory, by Foster Wheeler Corporation, under Contract No. 68-03-3255. September 1986.

EVALUATION OF PERSONAL COOLERS AND VITAL SIGNS MONITORS FOR HAZARDOUS SUBSTANCE CLEAN-UP OPERATIONS

By: W. Thompson Lawrence, Sc.D.
Carla Mond
Arthur D. Little, Inc.
20 Acorn Park
Cambridge, Massachusetts 02140

Raymond Frederick
U. S. Environmental Protection Agency
Hazardous Waste Engineering Research Laboratory
Woodbridge Avenue
Edison, New Jersey 08837-3679

ABSTRACT

Field tests were conducted in EPA's Region VII during the summer of 1986 and 1987. The operation studied was the bagging of dioxin contaminated soil while wearing Level "C" protective clothing. The objectives were to:

- evaluate various methods of obtaining vital signs of field workers;
- evaluate the feasibility of increasing productivity by using personal coolers to reduce heat stress.

Environmental and physiological parameters were measured. Results of these tests indicate that use of personal coolers can enable individuals to work for substantially longer periods of time at relatively high ambient temperatures. In addition, recommendations were developed for daily monitoring of worker vital signs at the beginning and end of each work day.

BACKGROUND

Under the direction of Dr. Ralph Goldman of Multi-Tech Corporation, two field tests were performed at hazardous waste sites in Region VII. During these field studies, workers were observed as they performed the "bagging" operation associated with dioxin clean-up. During "bagging", two individuals stand beside a hopper with arms upraised, holding a bag in position as a front-end loader operator moves contaminated dirt into the bag. Once the bag is filled, the baggers tie it, and the crane operator moves the bagged dirt to another area. During the operation, Level "C" protective clothing is worn: Tyvek coveralls with a hood, a full-face respirator, rubber gloves and boots, and a hard hat.

The first field study, which took place in Fenton, Missouri during the summer of 1986, provided data on the effectiveness of different automated vital signs monitoring techniques in measuring heat stress danger in a field environment. The second study, at Castlewood, Missouri during the summer of 1987, was undertaken to evaluate the use of selected personal coolers in increasing productivity in field activities, by reducing heat stress.

OBJECTIVE AND SCOPE

The objectives of the field studies were:

- to evaluate various methods of obtaining vital signs of field workers; and
- to evaluate the feasibility of safely increasing productivity by using personal coolers to reduce heat stress.

These evaluations were uncontrolled field trials, and the following limitations applied:

- the pacing and exact nature of the work each day could not be controlled;
- climatic conditions were variable;
- participation was voluntary.

METHODOLOGY

The data collection procedure and physiological data collected were slightly different for each study. The discussion that follows describes the type of instrumentation used and the protocol followed for each test.

INSTRUMENTATION

The instrumentation consisted of a computer data acquisition system for on-line data acquisition, meteorological instrumentation, physiological instrumentation, and personal coolers. All instrumentation was calibrated and then assembled for a "dry-run" in the climatic chamber at Multi-Tech. The equipment was then disassembled and shipped to the field sites.

The meteorological instrumentation included: air temperature (Ta), relative humidity (RH), solar load, black globe temperature (Tg), natural wet bulb temperature (Tnwb), wet bulb globe temperature (WBGT), and wet globe temperature (WGT). The air temperature was measured with Yellow Springs No. 405 air temperature sensor. Relative humidity was monitored with a dew point hygrometer manufactured by Yellow Springs. The solar load meter was Dodge Product No. 776. To obtain black globe temperature, a thermocouple was inserted into a 6 in diameter black globe. The natural wet bulb temperature was collected from a thermocouple covered by a wet cotton wick. A standard Botsball was used to obtain the wet globe temperature. Thermocouples were used for all temperature measurements and were automatically recorded by a Hewlett-Packard 9807A data acquisition system. The solar load readings were recorded manually.

The physiological instrumentation included skin temperature thermistors, heart rate monitors, body weight scales and, for the 1987 study, rectal temperature thermistors.

A three-sensor array with a connecting cable was used to determine the skin temperature at the chest, forearm, and calf of each subject. During the 1986 field study, a fourth temperature sensor was used to measure the medial thigh temperature. Based on the results of this study, the medial thigh temperature was not measured during the 1987 evaluation, and the fourth thermistor was used to measure the temperature of the personal cooler.

Four types of heart rate monitors were used in the 1986 study: a telemetering unit, a "BATON", an electronic heart rate/blood pressure device, and a manual count. The manual determination involved counting the number of beats over a period of at least 20 seconds. The other three monitors counted the interval between beats, picking up the signal generated at the skin surface by the electrical activity of the heart or generated as a peak in the blood pressure, and calculated the corresponding rates in beats per minute.

Monitoring body weight changes, day to day and between work shifts provided information about the risk of heat illness as a result of the integrated effects of work pace, ambient environment and clothing worn. A laboratory precision balance was used to measure the fluid intake of participants. A battery-operated, digital read-out scale was used to monitor the participants' body weight.

In the 1987 field study, personal coolers were introduced. The ice vest was supplied with a separate jacket designed to be worn over the vest to reduce heating of the ice by hot, ambient air. However, the jacket was not used in the test program. The vortex cooler was equipped with perforated hoses that supplied cool air to the arms and legs.

PROTOCOL

1986 Field Study

Preparation of Test Subjects--

Five workmen were selected to participate in the study. Four were baggers, and the fifth was the front-end loader operator. All five men reported to a dressing room early each morning and immediately after lunch to don the necessary protective clothing and the required instrumentation. They were weighed nude, the four skin temperature sensors were affixed, and the heart rate telemeter donned. They dressed and were reweighed "clothed" wearing the protective overgarment; the weight of the sensor harnesses and clothing ranged between one and two pounds. Some of the workers wore just shorts and a T-shirt underneath the overgarment, but one wore a long-sleeved, cotton flannelette shirt and blue jeans because he "did not like the feel of the overgarment against his skin".

The skin thermistors were attached to provide the mean weighted skin temperature (MWST). The first was placed on the upper chest (T_{chest}), roughly an inch above and two inches medial from the nipple. The second thermistor was placed on the inner aspect of the forearm mid-way between the wrist and elbow (T_{arm}). The third thermistor was affixed in the middle of the back of the calf over the bulge of the gastrochemius muscle (T_{leg}); and the fourth skin temperature (Test) was obtained by affixing the last sensor about 2 inches above the knee on the inner thigh. The conventional Burden 3-point MWST was calculated as follows:

$$MWST = .5\ T_{chest} + .34\ T_{leg} + .16\ T_{arm}$$

Since it has been suggested(1) that the thigh temperature is the best single-point representation for mean weighted skin temperature in the heat, this value was collected for comparison purposes.

Vital signs monitors were checked and "investigator baseline VSM readings" were taken on each subject using the "BATON", the telemeter unit and the electronic heart rate-BP instrument. The portable Yellow Springs Instrumentation Telethermometer box was used to read the thigh temperature.

Prior to initiating the study, each subject was instructed to drink only from his assigned container. Values for fluid intake, body weight, heart rate and completed bags, were recorded manually during the study and tabulated later.

Procedures--

The two "baggers" worked at either side of the "hopper" platform. They adjusted the inner plastic bag, holding it up against the throat of the hopper, prior to dirt being deposited from the front-end loader. The front-end loader operator had a slightly higher average workload than the baggers due to the constant shifting of body position in response to variation in the position of the front-end loader.

After approximately one hour (at the discretion of the Riedel Company Health and Safety Officer), the first two baggers moved to the rest area. There, a wooden bench was set-up on a rough wood pallet over which a tarpaulin had been erected on a crude frame to shield them from the sun. The second pair of baggers replaced them at the hopper.

As soon as possible, after the first two baggers had moved to the rest area, removed their respirator, and unzipped (and sometimes dropped their protective coverall to below their knees), an intensive "round robin" of heart rate and blood pressure measurements was initiated by Dr. Goldman and the Riedel Company nurse. These measurements, plus the nurse's reading of oral temperature, were taken sequentially for about fifteen minutes and provide the primary data base for comparison of the simple field VSM's with the conventional heart rate and blood pressure determinations.

The first team of baggers then rested and performed light work at the site, such as preparing bags, until shortly before the second pair were due for their rest break. They then donned their full protective overgarment and respirator and moved to their original work stations while the second pair of baggers moved to the rest area to begin the "round robin" evaluation of their vital signs.

When the work was done for the shift, the workers returned to the dressing room and were weighed fully clothed and nude. The time at which the weights were taken was recorded. Final drinking fluid bottle weights were also obtained.

1987 Field Study

Preparation of Test Subjects--

Four workers from the clean-up contractor's work force were used as test subjects during the evaluation. Program participation was voluntary and monetary incentives were used to solicit program participation. All participants were briefed as to the purpose of the study, the types of coolers being introduced, and the monitoring techniques.

The four volunteer workers were split into two separate work teams (A and B) which participated in the study on alternate days (e.g., Team A Week 1 W-F, Week 2 T-Th; Team B Week 1 Th-Sat, Week 2 M-W).

The test subjects were asked to report to the test site roughly one hour before the start of their afternoon work shift. Both workers were weighed nude and then outfitted with five thermistors. Three of the thermistors were used to monitor a test subject's skin temperature. These thermistors were placed on the test subject's forearm, chest and calf in the same manner as in the 1986 field study. A fourth thermistor, of special design, was inserted into the subject's rectum and used to monitor core temperature. The fifth thermistor was used to monitor the temperature of the personal cooler. This thermistor was directly attached to the ice vest, or positioned in the main delivery tube of the vortex cooler. These thermistors were attached to a single plug connection which could be passed through an opening in the protective clothing and connected to a computerized data acquisition system. One worker was provided with a vortex unit and the other with an ice vest. Both workers then donned protective clothing consistent with Level "C" protection requirements.

Procedures--

Each worker consented to modify his work cycle from a normal cycle of one hour working and one hour resting to a single, three-hour work period, during which he alternately performed his tasks with and without the aid of a personal cooler. The workers were instructed that cooling would automatically be switched if their partner was experiencing deep body temperature in excess of 101.5°F, or skin temperature in excess of 96.5°F.

The actual length of time each test subject worked without the aid of a cooler was limited by his individual tolerance to heat stress. Whenever they decided that they could not continue to work unaided, their cooling device was turned on. Initially, cooling was provided alternately to the workers. However, due to the high environmental temperatures, cooling was sometimes provided to both workers at the same time.

Test subject skin temperature and core temperature were monitored and recorded at five minute intervals throughout the work cycle. Originally, heart rate was to be monitored with a telemetering device. However, the unit failed to work in the field because of interference from electric noise generated by the earth moving equipment. Thus, heart rate was monitored manually when possible without interrupting work flow. Body weight was measured at the beginning and end of the afternoon work shift. In addition, fluid intake was monitored.

RESULTS

1986 FIELD STUDY ON VITAL SIGNS MONITORS

Summary

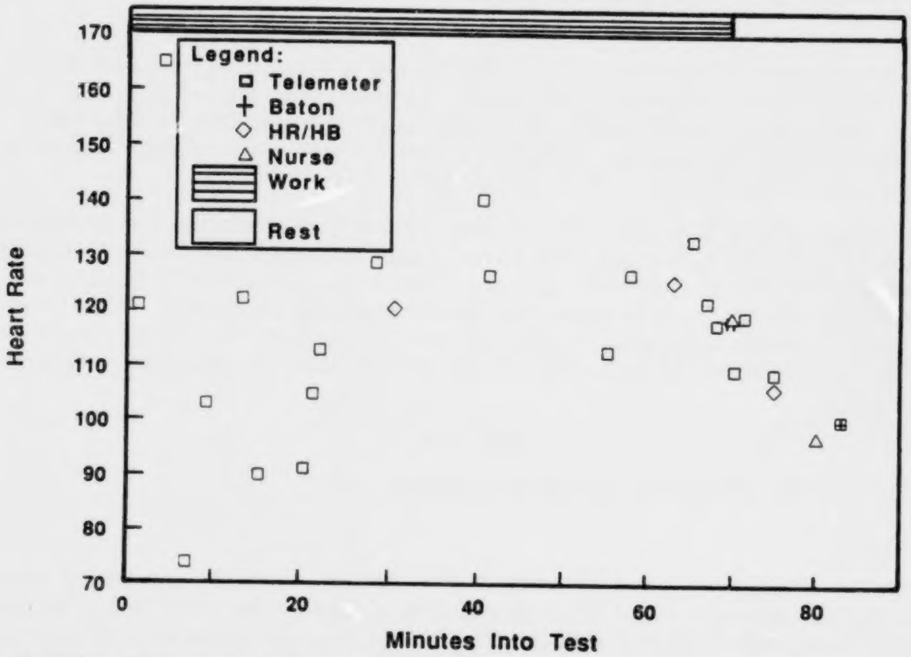
These tests provided data on the suitability of various devices for monitoring workers' vital signs during hazardous waste clean-up activities at dioxin sites. The results indicated that, for the work rates associated with the bagging task, skin temperature could be measured with thermistors attached to the chest, arm, and calf, weight could be measured using a digital "bathroom" type scale, and heart rate could be measured using a variety of inexpensive sports type monitors including a telemetered unit and a "baton" shaped unit held in both hands. No signs of heat stress were observed due to two key factors. First, the environmental conditions encountered during the tests were relatively cool (15-20°C temperatures with light solar loads around 100 Btu/hr - ft.^{2}) Second, the work rates were relatively low (estimated at 150-225 Watts).

Heart Rate Monitors

The units evaluated were:

- A telemetered unit in which a strap worn around the chest contained sensors and a transmitter which relayed the pulse rate up to 35 feet to a portable battery powered readout (Biosig #801).
- A baton unit which was grasped in two hands with a readout in the center (Biosig #103).
- An electronic, portable home-type blood pressure monitor with a heart rate readout (Marshall #85), and
- Manual readings taken by a nurse.

Data are shown in Figure 1. During the work period (indicated by the box above the data), heart rate moves erratically as different bagging related tasks are performed. In the rest cycle, the heart rate is more stable and approaches a resting value During the rest period, the monitors agree within a few beats/min.

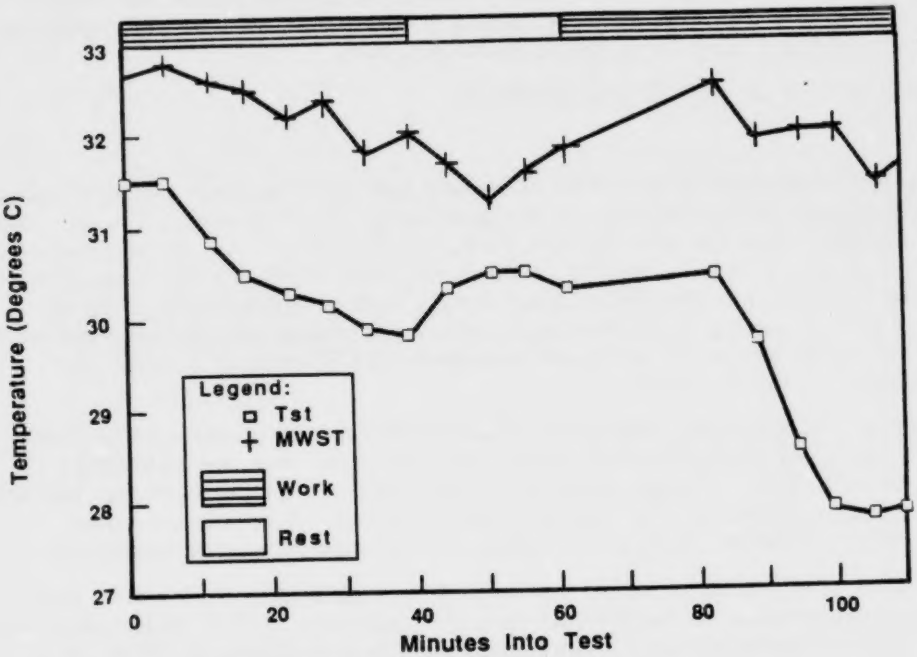


Bagging Task Indicates that Subject Is Working

FIGURE 1. COMPARISON OF HEART RATE MONITORS FRIDAY AM/MAN # 2

Mean Weighted Skin Temperature/Thigh Temperature

An example of data for these measurements is given in Figure 2. The MWST appears to correlate somewhat with the work/rest cycle. However, variations due to changes in work rate, dislocation of sensors, and orientation with respect to the sun also affect the data. This parameter is much less volatile than heart rate and therefore would be a more reliable indicator of heat stress if these problems were overcome.



Bagging Task Indicates that Subject Is Working

FIGURE 2. COMPARISON OF MWST AND THIGH TEMPERATURE WED. PM/MAN # 1

Thigh temperature was measured because it was believed by Dr. Goldman to be a single point value which would track the MWST. The data indicate that this was not the case for these test conditions. In addition, problems were encountered with this thermistor becoming dislodged particularly when the worker climbed up on the hopper to clear blockages.

Weight

Attempts at measuring sweat production by weighing clothes, fluid intake, and workers at the start and end of a shift and before and after urination/defecation were unsuccessful. Despite instructions to the contrary, workers shared water bottles, changed clothes, and urinated/defecated without notifying the investigators. However, the use of a digital scale to indicate day-to-day variations in a subject's condition provided useful information relative to monitoring heat stress risk.

Conclusion

Based on these results, it was determined that the appropriate instrumentation for monitoring participants during the 1987 field evaluation of personal coolers were MWST measured with three thermistors, heart rate measured with the telemetered unit, and body weight measured with a digital scale before and after a shift.

1987 FIELD STUDY ON PERSONAL COOLERS

Summary

These tests provided data on the use of ice vest and vortex personal coolers to reduce the risk of heat stress while enhancing worker productivity during bagging. The units tested were a Fyrepel Ice Vest #128 and a Fyrepel Vortex Cooler #167-5. The ice vest consisted of a jacket with pouches containing packets of chemicals previously frozen in a conventional freezer. The vortex cooler employs the Hilsch cooling method with compressed air to provide cool air to a cooling vest and through tubes to the extremities. The environmental conditions during the tests were varied and uncontrolled WBGT of 22.1°C - 32°C and relative humidity of 40.4% - 49.3%.

Results of the tests using these coolers indicated that the use of either could permit baggers to work safely and continuously for at least three hours with Wet Bulb Globe Temperatures up to 31°C. Without coolers in use, skin and core temperatures rose indicating that heat stress danger existed. When coolers were used, these temperatures declined indicating that their use should make continuous work possible under these conditions.

The telemetered heart rate system did not perform satisfactorily during these tests, possibly due to electromagnetic interference from the equipment. MWST measurement with thermistors was acceptable although sensors occasionally became dislodged. Their use required that the workers be tethered to the data acquisition system. Digital scales provided acceptable weight data.

Ice Vest Performance

The performance of the ice vests on a typical day is illustrated in Figure 3. During the tests, the subjects wore the vest until a new one was introduced, to avoid having to stop work to remove the used-up vest. The tests indicate that useful cooling is supplied for about 75 minutes. In Figure 3, the MWST falls initially and then begins to rise as the vest melts. The core temperature (rectal) drops slightly, lagging somewhat the MWST and then rises near the end of the cycle.

Vortex Cooler Performance

Figure 4 presents data on the performance of the vortex cooler on a typical day. MWST and core temperature rise initially without the use of a cooler. When the unit is turned on the MWST begins to fall almost immediately while the core temperature levels off and then falls 15 to 20 minutes later.

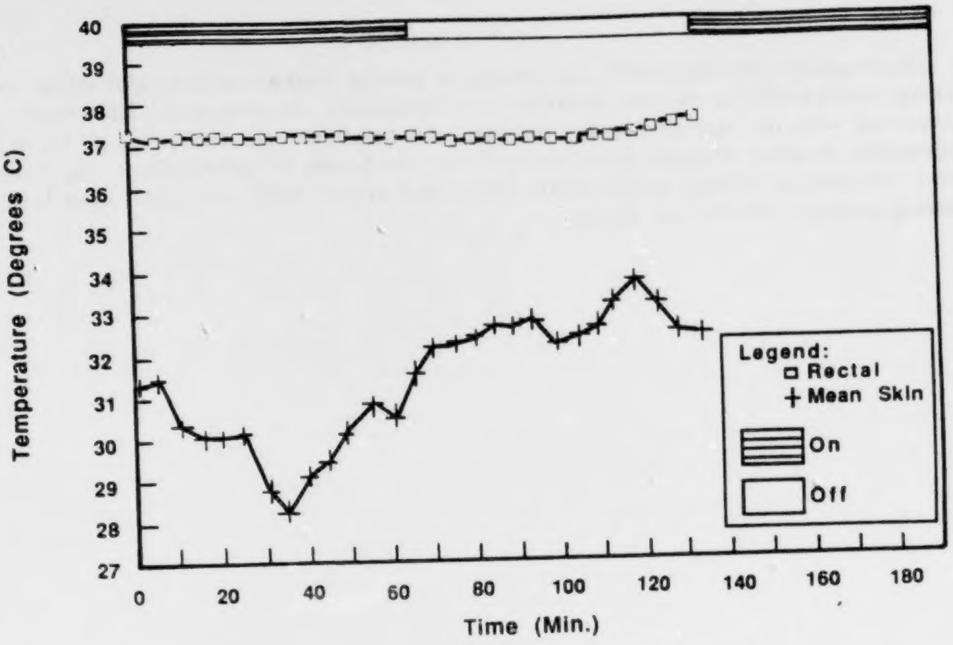


FIGURE 3. ICE VEST COOLER DAY 2

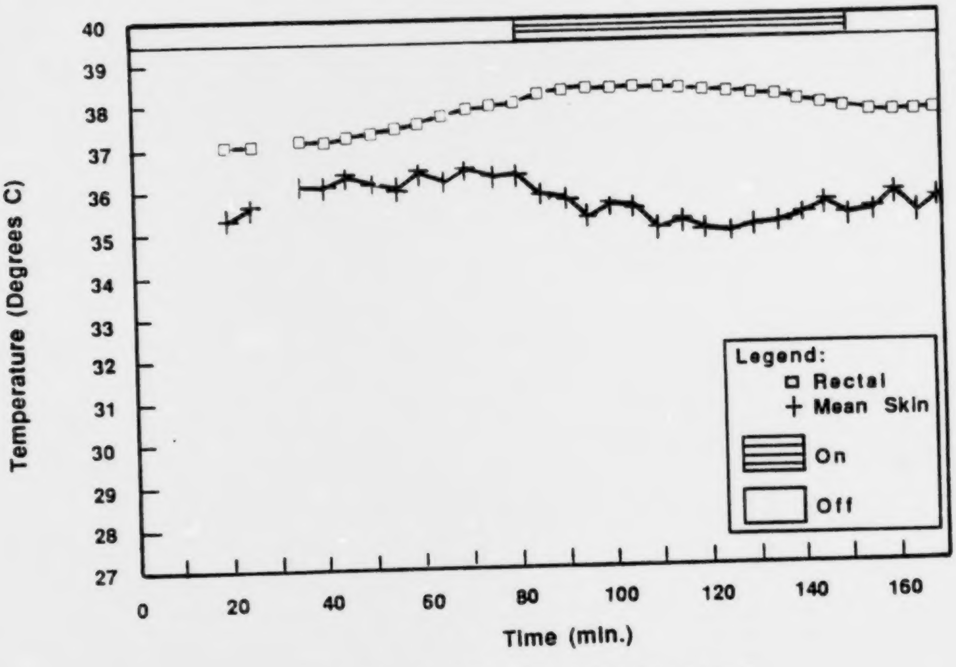


FIGURE 4. VORTEX COOLER DAY 4

CONCLUSIONS

Both coolers provided sufficient cooling to protect workers against heat stress while working continuously at the test environmental conditions. In these tests, difficulties encountered with the instrumentation indicated that improved equipment would be needed to continuously monitor workers, particularly if they could not be tethered to a data collection system. Monitoring worker weight daily, before and after a shift provides a basis for assessing potential risk to heat illness.

USE OF COLLOIDAL GAS APHRONS FOR IN-SITU BIODEGRADATION OF CONTAMINATED GROUND WATER

By: Donald L. Michelsen
Jeffrey W. Smith*
James A. Suggs**
Department of Chemical Engineering, Virginia Tech
Blacksburg, VA 24061

Credits: Project Funded Through Cooperative Agreement CR-813528-02-0
with Joint US E.P.A./Cinc and U.S.A.F. (AFESC-Tyndall) Support
Dr. Ron Lewis and Captain Ed Heyse, Project Administrators

ABSTRACT

Laboratory and pilot scale work has been conducted on the scale-up of generation, and the application of a 50 to 65% dispersion of stabilized microbubbles for hazardous waste treatment. A portable test facility has been designed, fabricated and successfully tested using a packed bed of millimeter sized glass beads to generate 40 l/min of the microbubble dispersion with bubbles less than 90 microns in diameter. Microbubble physical properties have been characterized and standardized through the development of improved photographic and analysis methods to determine size distribution, and through the development of a phase separation technique to quickly determine a measure of stability and quality (% air in dispersion).

The use of this stabilized microbubble dispersion as a potential oxygen source for in-situ biodegradation of flowing ground water has been studied in a vertical slice test cell 7 ft. x 7 ft. x 5 in. from front to back. A 50 to 65% dispersion of 50 ± 40 micron air bubbles has proven to be a feasible means for delivery and retention of supplemental oxygen in the saturated subsurface of sand as well as a simulated alluvial fan material. Downgradient dissolved oxygen measurements in the flowing ground water have verified continued oxygen transfer from the retained bubbles to the flowing ground water. The microbubble dispersion has proved superior in retention and delivery compared to sparged air/water injections. At least 25% of the oxygen in the microbubble is accounted for in the DO increase as anaerobic groundwater flowed through the treatment zone. This utilization could approach 50%, but about one-third of this oxygen retained is required to biodegrade the surfactant used to form stable microbubbles.

---

* Now with PPG Corporation, Cleveland, Ohio

** Now with DuPont Corporation, Savannah River Plant

INTRODUCTION

Aqueous foams are being used successfully throughout industry, especially in the areas of flotation, dust suppression, petroleum production, and fire fighting. However, the development of techniques for producing consistent fine microbubbles could expand applications and perhaps improve the uses of foams in industry. One new microbubble foam development is known as Colloidal Gas Aphrons (CGA). The name "aphron" comes from the Greek "αφρον", a foam, and has been coined to mean a fluid encapsulated in a thin aqueous shell, or true bubble. First investigated by Sebba (1972), CGA are typically characterized as a highly stable, 50 to 65% dispersion (quality) of 50 micron sized bubbles. Quality is defined as the % air as microbubbles in the total dispersion of air plus liquid. Thus a 65% quality means 65% air bubbles dispersed in 35% water. CGAs are typically a "wet" foam, meaning the air content is less than 70% of the total volume, which allows the bubbles to be far enough apart that no distortion is present. Because of their stabilized nature in part the result of 200 to 500 ppm surface active agent present, the individual bubbles do not coalesce. CGA viscosity is about 10 centipoise (cp) at room temperature although as the air content rises to 70%, the viscosity approaches 30 cp. These wet foams can be pumped with selected positive displacement pumps.

In contrast, dry or conventional foams usually are characterized by a high percentage of air, typically 95%, and the presence of distorted, polyhedral cells of much greater size than wet foams. The wet foam behaves like pseudoplastic fluids from 70% down to 50% quality CGAs. As the foam qualities drop below 50%, they behave like Bingham plastics; that is , a certain stress must be applied before any flow starts. The wide range of potential applications for these wet microbubble foams has been identified and include: flotation separation processes (removal of ash forming material from coal, algae from waters), enhanced oxygen transfer (high surface area) in gas-liquid systems (yeast generation in bioreactors), removal of oils from sand (scouring), and, use as an in-situ oxygen source (in-situ biodegradation of hazardous wastes).

Considerable CGA laboratory testing and some pilot-scale testing has been completed to address these applications. However, large scale testing has been restricted by the inability to produce larger quantities of these microbubbles. CGA generation has been limited to a technique known as the spinning disk method. This method involves the use of a small 1 to 2 in. flat disk rotating in excess of 4000 RPM between two carefully positioned baffles in a 2 liter beaker filled with dilute surfactant solution (Sebba 1985). With an overflow arrangement, this generator can operate in the continous batch mode producing up to 4 L/min of CGAs. Efforts to scale-up the spinning disk method have been hampered by the problem of generating the necessary high shear in larger vessels. Thus, the first thrust of this effort supported by USAF/EPA has been to develop and scale-up means for generating production quantities of CGA's and to quantify CGA characteristics.

For the treatment of hazardous waste and fuel releases to the ground environment, conventional technologies involve pumping contaminated groundwater to the surface for treatment. Since the solubility of organic pollutants in water is very low, and organics tend to be sorbed or occluded in soil, the flushing process can take decades. In situ technologies take the treatment process to the source of contamination and have the potential of accomplishing treatment faster. Enhanced aerobic biodegradation is theoretically effective for treating nonchlorinated organics. Biodegradation rates are limited by the availability of certain chemicals, particularly oxygen limiting chemicals, are added to the subsurface. Sparged air and hydrogen peroxide have been used to supply oxygen to the groundwater. Air sparging can only supply low concentrations of oxygen to water. Hydrogen peroxide is expensive. It also tends to degrade so rapidly in an aquifer that oxygen is lost from solution of hydrogen peroxide concentrations exceed 100 ppm.

This phase of the project investigated the potential to deliver a microbubble dispersion (versus sparged air/liquid mixture) to the saturated zone of an unconfined aquifer as the oxygen source for biodegradation of a hydrocarbon contaminant. The experiments involved a series of oxygen supplying injections to flowing ground water in a 7 ft. by 7 ft. by 5 in. deep (front to back) vertical slice. The thrust of this second study was to quantify the movement of these microbubbles through the soil matrix transported by the flowing groundwater and to study the retention, and cohesive properties of microbubbles (versus sparged air) and their propensity to form an active oxygen treatment zone.

BACKGROUND

Continuous Microbubble Generation

Currently the spinning disk technique (Sebba 1985) with its ability to generate 4 L/min of CGA using a continuous overflow system has become the standard CGA generation technique. This technique can provide sufficient quantities of microbubbles for laboratory and pilot testing. Other techniques for generating wet foams, gas sparging, and more recently high shear generation techniques have received attention. Dissolved air generation techniques also produce microbubbles of 40 to 150 micron size, but their quality is normally limited to only 5 or 10%. Sparging is still very popular for many application, but for the most part bubble size is 1000 microns (1mm) or greater unless shearing occurs. A number of shearing devices have received attention. Deister Concentrator has used a venturi approach to produce 40 to 50 micron bubbles (Parkinson, 1986). Shea and Barnett (1979) have described an idea for obtaining microbubble foam by using a hydrocyclone to separate the fine bubbles from conventional foam. More recently Professor Jan Miller at University of Utah has been testing an air-sparged hydrocyclone with a jacketed porous-wall tube to produce a 30 micron bubble size directly in the flotation reactor, and R. Yoon at Virginia Tech has been producing 100 micron bubbles in a continuous benchscale column (Parkinson, 1986). Finally Foot et al. (1985) and McKay et al. (1987) have been using an external bubble generator which produces bubbles less than 200 microns and larger by a combination of pressure dissolution and mechanical generation in a packed bed reactor. Much of the recent effort in microbubble generation has come from the interest in fine coal flotation/beneficiation, and most recent testing aims at producing a 80 to 95% quality dry foam.

After some consideration, we decided to study the system developed by Don Foot and Jeff McKay with the Bureau of Mines. The goal was to scale up a fine glass sphere packed bed system, and conduct testing to produce a 45 to 70% quality foam under conditions of high velocity (shear) and with concentrations of surfactant greater than the typical 5 to 25 ppm used for flotation.

The key parameters considered during this study were mean glass sphere diameter (D_p), Reynolds Number (velocity), quality of microbubble dispersion generated, and sodium dodecyl benzene sulfonate, (surfactant) concentration.

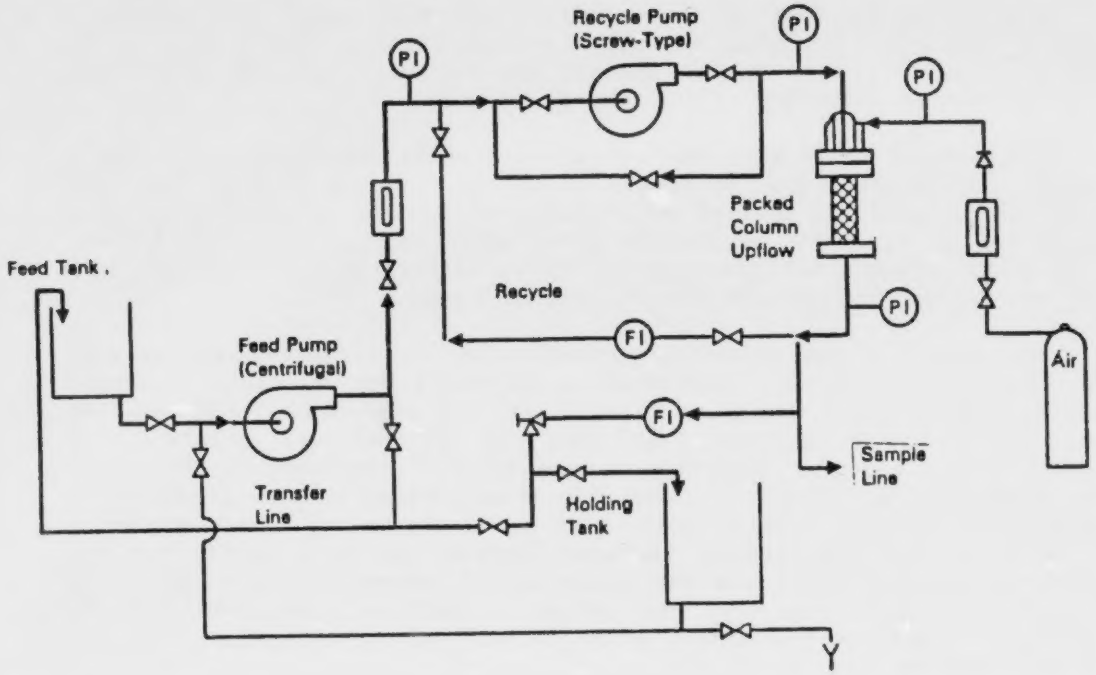
OXYGEN DELIVERY TO THE SATURATED SUBSURFACE

In the laboratory, Michelsen et al. (1984a) demonstrated that colloidal gas aphrons, when sparged into various unconsolidated saturated soil matrices, are "captured" and retained for prolonged periods of time. During these tests, 70 to 82% of the air incorporated into CGA's, made using a nonionic detergent (Tergitol 15-S-12), immediately adhered to a saturated coarse sand when sparged into the sand with a fork-like probe. Thirty days later, 70 to 80% of the initially captured microbubbles were still retained in the saturated sand matrix as an air dispersion or as coalesced aphrons. Similar tests were completed in a pilot test using a sand-filled trough with results of somewhat lower microbubble retention in the sand (Michelsen et al. 1984b, 1985). In similar tests, following the same procedures but injection air instead of CGA's, the air rapidly "bubbled up" and burst through to the surface with little gas retention in the sand. These studies suggest that in situ biodegradation could be enhanced using a combination of CGA's and nutrients injection into a saturated aquifer matrix to activate the indigeneous microorganism culture. A CGA injection study was conducted in a vertical slice test cell. The microbubbles showed a lack of lateral movement in the medium sand tested. The results suggest that in situ use of CGAs might be effective in a scheme where a dispersed screen of microbubbles would be injected to serve as a treatment zone through which the contaminants flow and are biodegraded (Michelsen et al. 1986, 1987).

EXPERIMENTAL AND RESULTS

Continuous CGA Generation

To conduct the CGA generation tests, a portable unit and upflow packed bed devise was designed and fabricated, see Figure 1. Air was added at several points in the generator prior to passing into the packed bed. The portable unit included means for sampling to check quality (% air in the



Recycle Pump
(Screw-Type)
PI
PI
PI
Packed
Column
Upflow
Feed Tank .
Recycle
PI
FI
Feed Pump
(Centrifugal)
Air
FI
Sample
Line
Transfer
Line
Holding
Tank

FIGURE 1. Portable Pilot Unit for Generating Microbubble Foam

total dispersion), stability (normalized rise % of clear liquid/bubble interface to foam disappearance), and bubble size and distribution. The microbubble dispersion sample line passed through a small viewing cell mounted on a 10X microscope. The image was picked up with a black and white videocamera and observed on a black and white high resolution TV screen. To record, flow was stopped and the image was photographed. A Kontron image analyzer was used to determine the bubble size and distribution from the microphotographs (Suggs, 1987).

Table 1 shows the results of testing with water flow rate as the variable. The stability increased with flow rate as evidenced by the lower interface height after 1 minute. In addition the greater number of smaller bubbles of less than 30 to 90 microns and fewer bubbles greater than 210 microns clearly show increased generation of microbubbles with increased flow rate (turbulence, shear).

Table 2 shows that as the quality increases again the stability improves and generally small microbubbles were formed. The generation of smaller microbubbles at higher quality was not expected, and additional testing would be necessary to clarify the results.

A number of tests with smaller sized packing were conducted, and a general trend toward smaller bubble sizes and improved (lower) stability was noted. Traded off against smaller microbubbles was pressure drop which increased, as expected, as smaller glass spherical packings were tested. An important element not investigated during testing was the void air (non bubbles) passing through and not observed as bubbles.

The effect of surfactant concentration on bubble generation was also evaluated. As surfactant concentration increased the stability increased and the bubble distribution was altered. At low surfactant concentrations the proportion of bubbles less than 30 microns was greater. As concentration increased generally a more bimodal distribution of smaller and larger bubbles appeared although the proportion of bubbles greater than 210 microns dropped. Some distortion in the analysis may have occurred as a result of the long tubing distance between the test system and the microscope mounted cell, and the selection of images on the screen to be photographed(sample size was not large). Additional studies would be desirable to explore the effect of surfactant level particularly on size and distribution data.

The effect of 0.9 recycle ratio on microbubble generation with the presence of the packed bed was also studied. The recycle ratio is the fraction of microbubbles returned to the inlet of the recycle pump compared to form (product) going to the holding tank. The stability (interface height at one minute) was 25 and considerably lower than the stabilities on Tables 1 and 2 and approaching the stability of 10 to 12 (1 min) observed for CGAs generated with the spinning disk generator. Also with the recycle pump (Allweiler Pump Co., screw type positive displacement pump) the faction of bubbles less than 90 microns was 96.4%.

In summary, the packed bed can be used to scale-up and produce larger

TABLE 1

EFFECT OF WATER FLOW RATE

Stability (500 mL cylinders)

Run	Water Flowrate (L/min)	Quality	Interface height at: 1 min	2 min	Slope
5	12	65.6	80	88	8
6	16	62.8	77	87	10
7	20	61.7	70	82	12
8	24	62.2	63	78	15

Size and Distribution

Run	Peaks (μ)	Bubbles < 30 μ	Bubbles > 210 μ	Fraction < 90 μ (%)	Number of Bubbles
5	45, 105	0	8	31.8	44
6	105,195,45	0	6	26.2	42
7	45, 165	6	6	50.9	53
8	45,105,195	3	3	46.2	52

Concentration = 500 ppm of NaDBS
Packing Diam. = 1.5 mm
Recycle Rate = 0

Peaks : Midrange value of size range eg. 45 μ = 31-60 μ. Listed from largest to smallest.

TABLE 2

EFFECT OF QUALITY

Stability (500 mL cylinders)

Run	Quality	Interface height at: 1 min	Interface height at: 2 min	Slope
11	53.6	83	92	9
7	61.7	70	82	12
12	72.3	46	67	21

Size and Distribution

Run	Peaks (μ)	Bubbles < 30 μ	Bubbles > 210 μ	Fraction < 90 μ (%)	Number of Bubbles
11	45,105	4	7	40.3	62
7	45,165	6	6	50.9	53
12	15,135,205	38	0	68.9	122

Concentration = 500 ppm of NaDBS
Feed Flowrate = 20 L/min
Recycle Rate = 0
Packing Diam. = 1.5 mm

Peaks : Midrange value of size range, e.g. 45μ = 31-60μ.

quantities of microbubbles. A column packed with millimeter sized glass beads is able to produce an effective microbubble foam that contains a majority of bubbles less than 90 μ, and few greater than 150 μ. The ideal operating conditions for producing these microbubbles are as follows: any feed flowrate from 12 to 24 L/min; foam quality of 65% (34-68 L/min of microbubble foam); surfactant solution of 200 ppm NaDBS; bead size of 3.0 mm: and, a recycle ratio of 1.0. If the inclusion of a few large, 200 to 300 micron sized bubbles does not affect the application for which the product will be used, operation without recycle is recommended. For this case, operating conditions require 20 L/min or more feed flowrate, 65% foam quality (57+ L/min of microbubble foam), 200 ppm NaDBS, and a bead size of 1.5 mm.

The operation of a packed bed microbubble foam generator was both feasible and reliable, and economically viable. The estimated operating cost is $0.58 to provide 1800 L/hr of bubbles using pressurized dissolved air techniques with a continuous flow system. Cyclic batch flotation systems could be cheaper. Dissolved air flotation (DAF) techniques are widely used in the food, mineral, and petroleum industry for removing particulates and dispersed oil from wastewaters. However, the operating cost is $.35 ($.33 for surfactant, 250 ppm solution) to provide an equal volume of microbubbles using the packed bed generating system (Suggs, 1988). The major concern, however, is that the packed bed generator will plug if wastewater effluent containing solid matter is used for bubble generation (typical operations). Current work is underway to minimize surfactant utilization (cost) and the development of a new non-plugging CGA generator.

IN SITU

The on-going research in the vertical cell has been evaluating the propensity for CGA's (versus sparged air) to flow through a saturated medium sand (10^{-2} to 10^{-3} cm/sec hydraulic permeability) and an even coarser alluvial fan consisting of a natural gravel/sand mixture layer larger than 100 mesh but passing a 3/8 in. screen (10^{-1} cm/sec hydraulic permeability). These studies have evaluated changes of dissolved oxygen in the flowing groundwater, movement of discrete microbubbles into the groundwater, and effect of treatment injection on water permeability (plugging) through the vertical test cell.

Figure 2 shows the front view of the vertical slice cell used for this study. The groundwater table maintenance was controlled by establishing the hydraulic head in the groundwater feed tube on left with groundwater effluent controlled by gravity overflow on the right. The solution feed tube served as the injector for intermittently or continuously introducing the microbubble dispersion or sparged air/water mixture. Details for control of ground water introduction, the CGA generation/injector system, and test cell sample matrix in the back face have been documented by Smith (1988). A spinning disk generator operating in a constant overflow mode supplied the CGA injection. Level indicator taps were tied into the manometers (piezometers) mounted to the right of the cell. A matrix of sample ports (back face) were used with quick release valves to withdraw

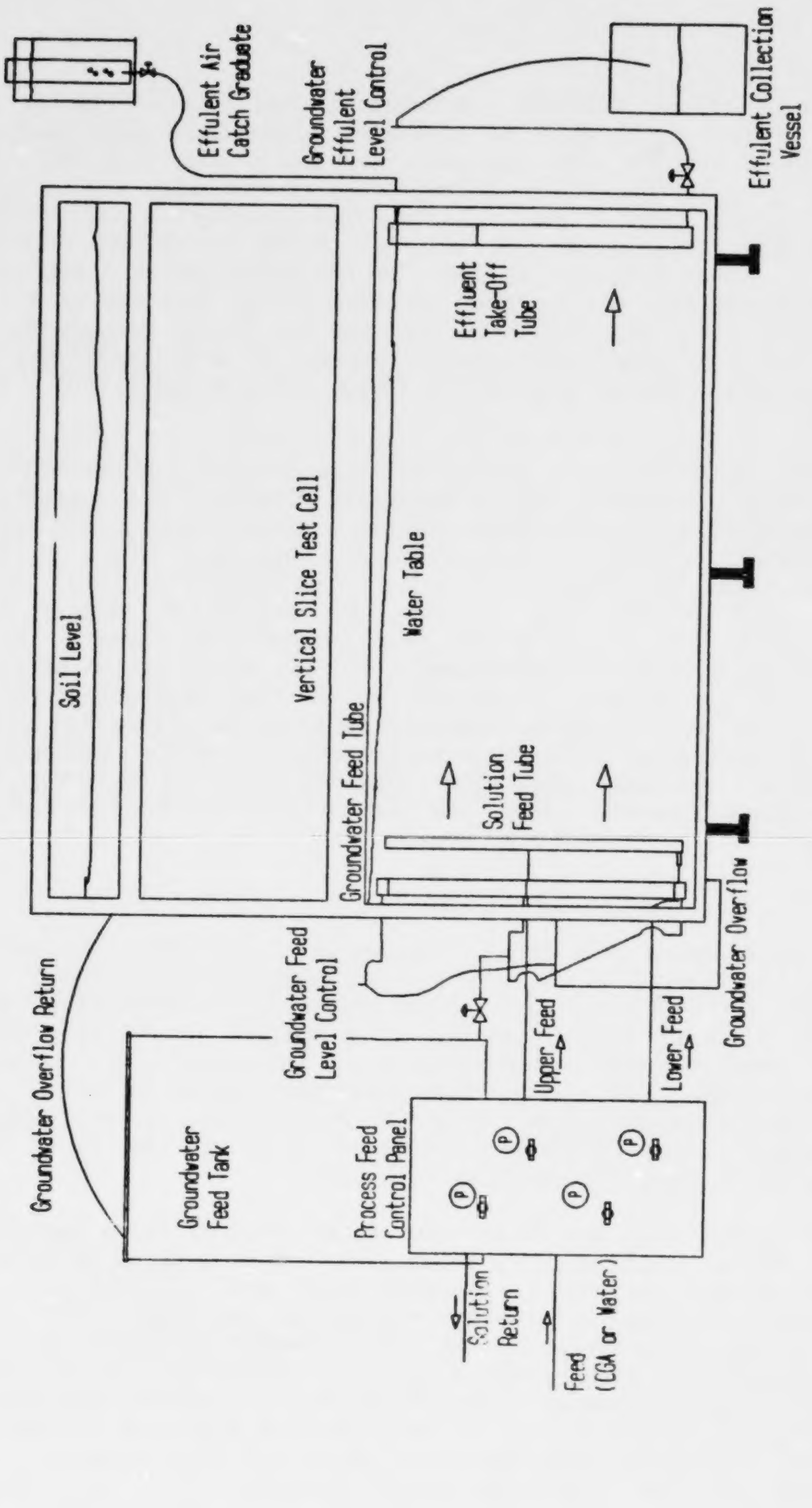

Effulent Air Catch Graduate
Groundwater Effulent Level Control
Effulent Collection Vessel
Soil Level
Vertical Slice Test Cell
Water Table
Effluent Take-Off Tube
Groundwater Feed Tube
Solution Feed Tube
Groundwater Overflow
Groundwater Overflow Return
Groundwater Feed Level Control
Upper Feed
Lower Feed
Groundwater Feed Tank
Process Feed Control Panel
P
P
P
P
Solution Return
Feed (CGA or Water)

Figure 2. Vertical Slice Test Cell Schematic

liquid samples for microbubbles, dissolved oxygen (D.O.), pH, temperature and for colorimetric analyses.

With either soil matrix tested the dissolved oxygen showed a sharp increase with a step introduction of a sparged air or CGA's into the gradient. With a medium sand matrix few microbubbles were observed down gradient after introduction of sparged air or CGA's, and in both cases, permeability changed little after injection. Based on laboratory studies we expected to see microbubbles traversing through the coarse alluvial sand matrix also tested in the vertical cell but few were observed. Instead, CGA air bubbles and sparged air bubbles/saturated water caused the D.O. downstream to increase. Figure 3 provides a profile of D.O. as a function of cell position during the 24 hours after an initial pulse of CGA injection. Groundwater flow was kept constant during the first 11.75 hours with a velocity of about 0.75 ft. per hour. The vertical dashed line shows the location of the groundwater wave front after pulse aeration assuming uniform horizontal groundwater velocity (plug flows) through the vertical slice. The flow was then stopped. Figure 4 provides a similar D.O. profile to above but with an initial pulse of sparged air/water injection. Groundwater flow for 8.5 hours after CGA injection was measured at a velocity of 1.1 ft. per hour before being turned off. During both pulse injections, some bubble and air loss was observed surging to the unsaturated zone. However, the remaining air and especially CGA microbubbles stabilized in place as documented in earlier testing. The fixed microbubbles supplemented the dissolved oxygen in the continually flowing groundwater passing around the injection sparger for over a day. The oxygen delivery of injected sparged air depleted much more rapidly, and was less effective in transferring dissolved oxygen to the flowing groundwater using a single pulse procedure Oxygen transfer for CGA injection to the flowing groundwater was determined by multiplying the groundwater flow (0.75 ft/hr) by the estimated ΔDO (4.0 ppm) pick-up measured at injection point for the duration of the 11.75 hr test. An estimated 0.140 g. moles were transferred. The total CGA bubbles injected were 7.2 L of air or 0.571 g. moles O_2 or a 25% oxygen delivery to the flowing groundwater.

The generation of microbubbles requires the use of a minimum 100 ppm surfactant concentration. (500 ppm were used in Run 10, Figure 2). With 3.0 liters of liquid injected (to form the wet microbubbles) and assuming a 1.0 mg O_2/1.0 mg surfactant is required for biodegradation of the surfactant, this means that 0.094 moles of the 0.140 moles injected/delivered oxygen (67%) could be required to biodegrade the surfactant used for generation. On-going aquarium injection studies have demonstrated that 50% retentions are realistic, so in practice perhaps 66% of the O_2 retained (33% of the oxygen supplied) would be available for pick-up and in-situ biodegradation of contaminants flowing through a treatment zone.

A similar calculation for the single air pulse gave only an average ΔDO of (1.5-0.5) or 1.0 and a 6.0% delivery of injected oxygen to the flowing groundwater. The efficiency is low but cost of continual sparging instead of pulse sparging is not high.

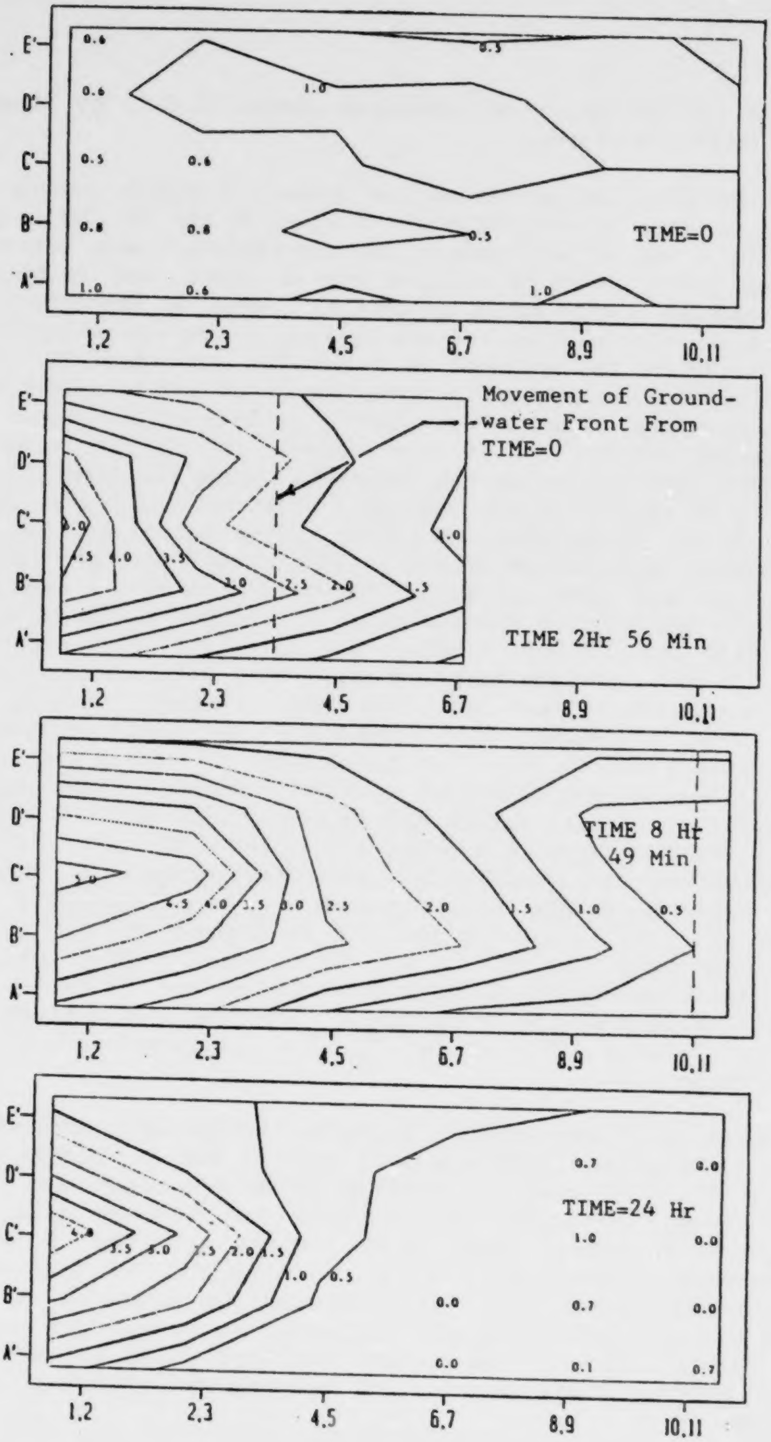


Figure 3

Dissolved Oxygen Concentration (mg/L) Within The Vertical Slice Test Cell Using Injected CGA Pulse, Run 10.

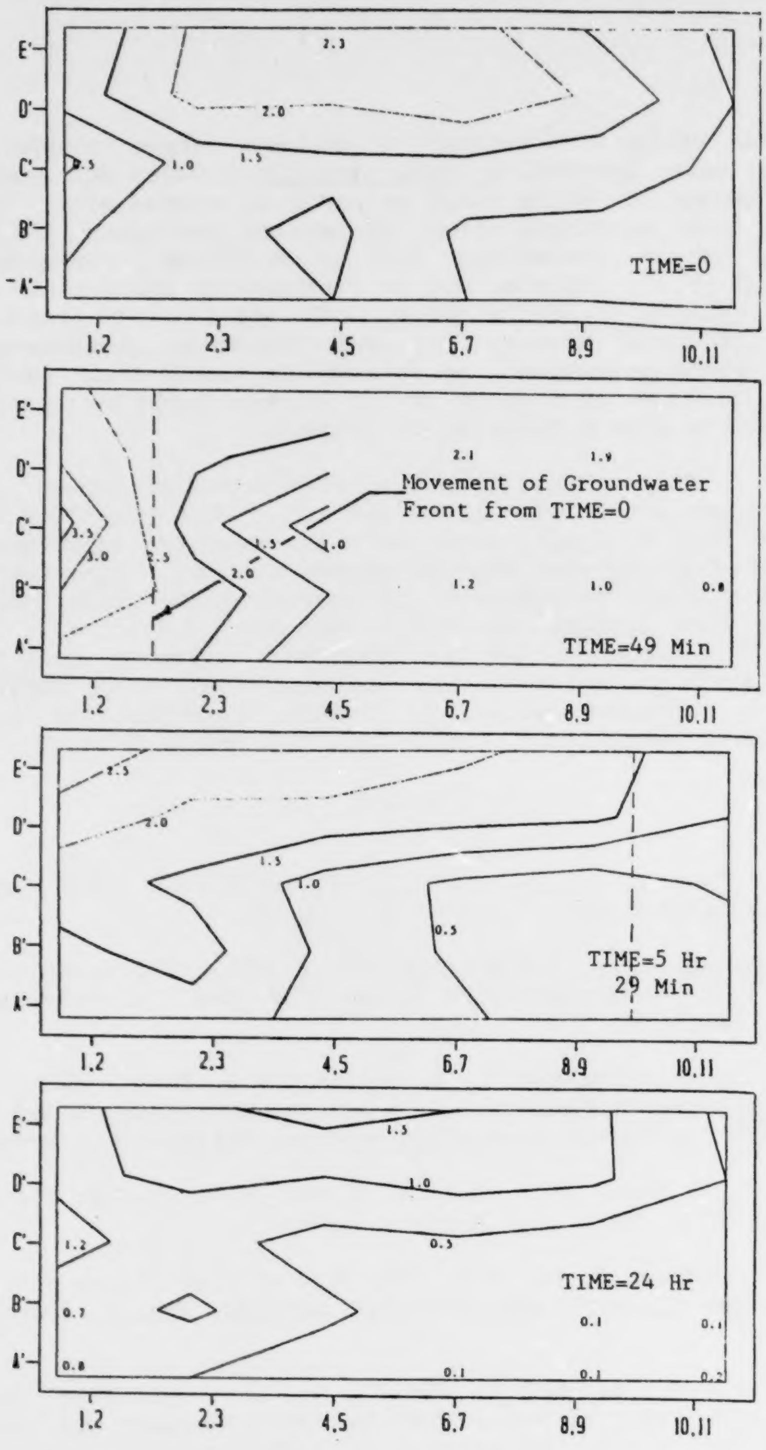


Figure 4

Dissolved Oxygen Concentration (mg/L) Within The Vertical Slice Test Cell Using Injected Air/Water Pulse, Run 7.

Subsequent testing will continue to evaluate oxygen transfer to the flowing ground water provided by intermittently injected CGA compared to continuously sparged air which could be justified economically. The CGAs will be made from non-biodegradable 3M anionic surfactant, FC-100, to eliminate the oxygen consumption due to surfactant biodegradation. Blockage formed by the injected CGA or continuously sparged air will be measured by injecting a solute pulse (NaCl addition) to increase the groundwater electrical conductivity and following groundwater flow patterns. If blockage occurred, no increase in conductivity would occur downstream of the point of blockage or the increase would be significantly reduced compared to when no blockage was present.

In summary, CGA, unlike sparged air/air saturated water, provided supplemental oxygen which formed an "oxygen wall." CGA accumulate near the injection tube in a stationary front which increased the dissolved oxygen concentrations of groundwater flowing through the cell. Dissolved oxygen data showed that CGA runs achieved consistently higher dissolved oxygen concentrations than sparged air runs. Overall utilization of charged oxygen was 25% assuming a 100 ppm surfactant solution used for CGA generation. Laboratory and small aquarium studies are being conducted to further reduce surfactant usage, to improve stability and injection procedures, and to design the configuration for a treatment zone.

Bibliography

Bird, R. B., Stewart, W. E., and Lightfoot, E. N., 1960, Transport Phenomena, John Wiley & Sons, New York, p. 200.

Foot, D. G., McKay, J. D., and Huiatt, J. L., 1985, "Column Flotation of Chromite and Fluorite Ores," 24th Annual CIM Conf. of Metallurgists, Vancouver, BC, Canada.

Fugate, E. J., D. L. Michelsen, D. A. Wallis and F. Sebba, 1985, "Use of Colloidal Gas Aphrons to Facilitate Decontamination of Subsoil Hydrocarbon Spills," Presented and preprinted, AIChE meeting, Chicago, IL, November.

Mackay, J. D., D. G. Foot, Jr., and M. B. Shirts, 1987, "Column Flotation," U. S. Bureau of Mines, Salt Lake Research Center.

Marsden, S. S. and Khan, S. A., 1966, "The flow of foam through shor porous media and apparent viscosity measurements," Soc. Pet. Eng. J. (March), pp. 17-25, AIME 237.

Michelsen, D. L., D. A. Wallis, and F. Sebba, 1984b, "The Use of a Microdispersion of Air in Water for In Situ Treatment of Hazardous Organics," pp. 398-403 in Proceedings of Fifth National Conference on Management of Uncontrolled Hazardous Waste Sites, Hazardous Materials Control REserach Institute, 1984.

Michelsen, D. L., D. A. Wallis and S. P. Lavinder, 1985, "In-Situ

Biodegradation of Dispersed Organisms Using a Microdispersion of Air in Water," pp. 291-298 in Proceedings of 6th National Conference on Management of Uncontrolled Hazardous Waste Sites, Hazardous Materials Control Research Institute, Washington, D.C., November.

Michelsen, D. L., D. A. Wallis and F. Sebba, 1984a, "In-Situ Biological Oxidation of Hazardous Organics Using Colloidal Gas Aphron Systems," Environmental Progress, Vol. 3, No. 2, pp. 103-107, May.

Michelsen, D. L., E. Fugate, D. A. Wallis, J. Fisher, F. Sebba and R. Paris, 1987, "In Situ Groundwater Mitigation of Hydrocarbon Contamination Using Colloidal Gas Aphrons," Final Report, American Petroleum Institute, Washington, D.C.

Michelsen, D. L., Wallis, D., & Sebba, F., 1986, The Use of "Aphron" Techinques for Treating Hazardous Wastes, 3rd Intl. Congress of Chemical Engineering, Tokyo, Japan: Sept.

Parkinson, G. (Reporter), 1986, "Improved Flotation Routes Get Separations Tryouts."

Perry, R. H. and D. W. Green, ed., Perry's Chemical Engineers' Handbook, sixth edition, McGraw-Hill, New York, NY.

Sebba, F., 1971, "Microfoams--an unexploited colloid system," J. Coll. Interface Sci., 35(4), pp. 643-6.

Sebba, F., 1985, "An improved generator for micron-sized bubbles," Chem. Ind., pp. 91-2, Feb.

Shea, P. T. and Barnett, S. M., 1979, "Flotation using microgas dispersions," Sep. Sci. Tech. 14(9), pp. 757-767.

Suggs, J. A., 1987, Generation of Microbubble Foam Using A Packed Column, Master's Thesis, Virginia Polytechnic Institute & State University, Blacksburg, VA, September.

EXPERT SYSTEMS TO ASSIST IN REVIEW OF CLOSURE PLANS FOR LAND DISPOSAL SITES

by: Daniel G. Greathouse
U. S. Environmental Protection Agency
Hazardous Waste Engineering Research Laboratory
Cincinnati, Ohio 45268

BACKGROUND

The Resource Conservation and Recovery Act (RCRA) of 1974 mandates that all hazardous waste land disposal facilities have an approved closure plan by the fall of 1988. Included under this requirement are all new hazardous waste land disposal facilities that have opened since 1974 in addition to those that were in operation at the time of enactment of the RCRA legislation. The principal objectives of these plans are protection of the environment from hazardous waste contamination and minimization of possible associated adverse health effects. To accomplish these objectives, the Agency or designated states must thoroughly review proposed closure plans for compliance with sound engineering principles and regulatory policies. Review consistency is also an important factor in implementation of this national regulatory requirement i.e., a closure plan should be evaluated similarly by all regulatory officials within and among the EPA regional offices and states. A package of four expert systems is being developed to aid in accomplishing the objectives of the closure plan for these reviews. Each expert system addresses a major component of a closure plan, namely final cover, leachate collection, run-on/off control, and vegetative cover. This paper will describe these four systems.

Closure plan review was identified as a high priority decision area in discussions with EPA regional office permit review staffs and the EPA Office of Solid Waste. Since relevant expertise and assistance was available for decisions relating to closure plan review, the topic was selected for development of expert systems. The Hazardous Waste Engineering Research Laboratory (HWERL) and CDM Federal Programs, under contract to HWERL, met further with Agency decision makers and outside experts to identify the specific closure issues amenable to expert systems development. Six issues, representing the major components of a closure plan, were identified; the components were final cover, vegetative cover, leachate collection, run-on/off, ground water monitoring, and long term maintenance. Development of expert systems to address two of these areas was initiated in 1987. Each expert system has been designed to operate as an independent module as well as in conjunction with the other systems. When used as a package the systems complement each other by sharing information and conclusions, thus increasing user productivity. These systems will be discussed in this paper.

MATERIALS AND METHODS

Expert systems are computer programs (software) designed to provide advice in specialized areas. The design objective of these programs is to emulate the advice of subject specialists by incorporating the experientially derived decision rules or criteria that they use. A common way of representing this knowledge is with IF---THEN statements. For example, see Figure 1. As the different types of knowledge or the number of decision rules increase, then more sophisticated knowledge representation techniques such as objects, frames, demons, or neural nets, may be required. Expert systems differ from traditional computer programs in several ways

1. Procedural versus goal oriented
2. Knowledge/judgment under conditions of uncertainty versus information manipulation
3. Separation of knowledge from inference mechanism and interface.

Expert systems offer the opportunity to effectively use state-of-the-art technical knowledge, operational experiences, and regulatory policies in evaluation of the complex issues associated with closure plans. A long history of relevant hazardous waste research in addition to operational experiences with different designs and site conditions have produced an extensive literature base and expertise resource. This information and these experiences can be synthesized along with the relevant regulations and policies into a decision aid via expert systems technology. Hence these tools are a means of providing ready access to a knowledgeable, consistent consultant for each permit reviewer in the ten EPA regional offices and the states with regulatory authority. The need for doing literature searches, review of relevant regulations, and/or contacting specialists with limited time is reduced. Hence these systems should reduce the time for evaluation of closure plans in addition to improving their quality. Other important benefits to the closure plan review process include training new reviewers and documentation of review decisions and the bases for them.

CDM Federal Programs under contract to the EPA Hazardous Waste Engineering Research Laboratory are developing the Closure Plan Review Advisory Expert Systems (Advisory CES). CDM has been responsible for each stage in the development process including identifying the key issues; determining the scope of the issues; collecting information from experts, regulatory personnel, and targeted users (knowledge engineering); development of the software; and field testing of the systems. An oversite group comprised of the ORD project officer and knowledgeable personnel from the

IF

1) 1) the post-subsidence convex slope of the vegetative layer is greater than or equal to 2, and

    2) the post-subsidence convex slope of the vegetative layer is less than or equal to 5, or

2) 1) erosion in tons per acre per year is less than or equal to 2, and

    2) 1) the post-subsidence convex slope is less than or equal to 33, or

        2 the proposed vegetative cover is nonvegetative,

THEN

it is definite that the slope of the vegetative layer is adequate.

Figure 1. Decision rule concerning adequacy of post subsidence slope

Office of Solid Waste (OSW) was set up to monitor the overall direction of these development efforts. The OSW staff has been reviewing each system to ensure compliance with regulations and their knowledge of the scientific literature. The systems are/have been being developed for use on an IBM PC/AT, or compatible, microcomputer with a minimum of 640k of RAM and a CGA graphics board with a color monitor. The PC Plus expert systems shell (developed and distributed by Texas Instruments) is being used in conjunction with PC SCHEME (a version of the Lisp language by Texas Instruments) to code the systems.

The focus of the closure plan review systems is review of plans for land disposal sites which are, or will be, closed as landfills. Hence decision issues unique to clean closures or partially clean closures for surface impoundments are not addressed. Also these systems do not provide advice for plans that differ from prescribed regulatory criteria and EPA guidance. For example, there is no advice for review of an alternative to a RCRA cap even if the applicant states that performance will be the same or better. Advice, beyond that included in EPA regulations and guidance, is limited to those situations and areas not specifically addressed by them.

Initiation of this development effort involved identification of the major closure related decision areas that would be amenable to expert systems development. Input was solicited from the targeted user community within EPA regional offices, EPA headquarters, and states with regulatory authority of hazardous wastes prior to area selection. It is very important that the resulting systems meet the needs of the targeted user community. The six areas selected for development were final cover, leachate collection, run-on/off controls, final vegetative cover, ground water monitoring, and long term maintenance. A guidance committee comprised of the work assignment manager, the ORD project officer and representatives of the EPA Office of Solid Waste was organized to guide development of the systems. The function of the guidance committee is to:

1. review the system prototypes during development
2. identify appropriate experts
3. review or identify other knowledge base reviewers
4. identify appropriate regulatory, guidance, and scientific documents
5. ensure the adequacy and compliance of the system conclusions with current regulatory policies and documents.

The first system selected for development is the final cover advisory system. The principal objective of this module is to determine whether a proposed cover system meets the regulatory criteria set forth in 40 CFR Part 264 for the closure of landfills and surface impoundments. Based on the recommendations of the Office of Solid Waste, the performance criteria specified in their guidance documents are used to evaluate a proposed final cover. This limits a cap to the standard "RCRA cap" endorsed by EPA. Hence the system verifies that the proposed cap is comprised of five layers; vegetative, filter, drainage, flexible membrane liner, and soil liner layers. For each layer, the system ascertains the acceptability of general design criteria such as slope, permeability, construction practices or limitations, and capacity to handle percolated fluids. The suitability of each layer is determined as an independent component as well as part of an integral system. Recommendations for approval (or disapproval) are provided which are based on characteristics of the waste, layer designs, filling practices, etc. The final cover advisory system determines if the cover design promotes drainage and if migration of waste to surface and ground water are minimized. This module is ready for extensive beta testing.

The second system examines some general issues concerning the vegetative cover including its slope and the potential for run-off to cause gullies in the cover. The system is broken down into three components; subsoil, topsoil, and vegetation. In evaluating the soil layers, the system first checks for appropriate textures and thicknesses. Properties of topsoil that are analyzed include the organic content, pH, conductivity, and percent of coarse fragments. Similar checks are done for the subsoil. The system evaluates the proposed vegetation by first asking the user for the state and season in which planting will occur. Once the plant species are identified, the system ensures that it is appropriate to plant each species in the specified state during the season indicated. Two data bases were developed to do this evaluation. Criteria for approval of the plant mixture include the elimination of any deep rooted species and the inclusion of at least one drought tolerant species and one perennial. All legumes are checked for inoculation. Finally, the system checks that the proposed method of application is specified and that mulch and seed rates are adequate. This system is currently in the demonstration prototype stage.

The third system is designed to evaluate a proposed or operating leachate collection and detection system for completeness and compliance with current RCRA requirements set forth in 40 CFR Part 264, 40 CFR Part 265, and in the Hazardous and Solid Waste Amendments of 1986. Performance criteria which appear in guidance documents are incorporated in the system to test for leachate collection system adequacy. Four elements of the leachate collection system are evaluated; clogging, leachate head, storm capacity, and pipe strength. The expert system determines whether the overall design meets the regulatory objective and whether there is a potential for failure in any segment of the unit. No attempt was made to incorporate requirements set forth in the proposed May 29, 1987, regulations for double liner systems. This system is ready for limited field testing by representatives of the targeted user community.

The fourth system is being developed to assist in evaluation of the proposed run-on/off control systems. It is assumed that the applicant has accurately interpreted the topography of the site and has properly designated drainage areas. The system determines if there is a potential for run-on, and if so, how it is being handled with respect to run-off. Of the run-on/off control structures, only the most down gradient conveyance and basin are evaluated by the system. This assumes a worst case scenario with run-on/off water reaching the most down gradient location. The user can ask the system to check the applicant's calculations for other run-on/off control structures, but in this case it is the user's responsibility to identify and track which conveyances and basins have been checked. For each conveyance, the system checks that the peak discharge flow is less than the conveyance flow capacity and that the fluid velocity in the conveyance is less than its threshold velocity. The volume of each basin is calculated. A checklist is also provided to ensure that the applicant has provided all the supporting documentation detailed in the run-on/run-off calculations. This system is currently under development.

Due to unexpected resource requirements for the first four systems, the fifth system, ground water monitoring, and the sixth system, long term maintenance, were not initiated.

Other expert systems are being developed by the Hazardous Waste Engineering Research Laboratory to provide assistance in the review of permits for land disposal facilities and to assist in Superfund clean-up activities. Issues addressed by the systems include evaluation of method 9090 data for flexible membrane liners, evaluation of waste analysis plans, screening of dike design features for surface impoundments, and screening of technologies for the clean up of superfund sites. All of the systems are operational. The first three are ready for extensive field testing and the fourth system is ready for review by experts.

DISCUSSION

Closure plan review was identified as a high priority decision area by an EPA sponsored requirements study for land disposal related expert systems, by permit reviewers in the EPA regional offices, and by staff involved with land disposal regulations within the EPA Office of Solid Waste. Recognizing this need for decision support and the availability of a large information and expertise resource, the area was selected for expert system(s) development. Component selection (final cover, leachate collection, etc.) was based on the recommendations of knowledgeable experts and the EPA regional office staff. Using instructions provided by the staff of the Office of Solid Waste, the systems were designed to comply with appropriate OSW guidance documents. For those situations where more than one guidance was available, the OSW staff specified which to follow. By keeping the closure plan rules within accepted OSW guidance, the systems were designed to meet the advisory needs of the users. Experts were used to interpret and expand the information in the guidance documents when necessary. In a limited number of cases when EPA policy was unclear, information provided by experts and not addressed by guidance were incorporated into the knowledge base. The entire content of all knowledge bases were reviewed several times by designated EPA staff.

In order for decision aids to be useful within a regulatory program they must synthesize both the regulatory requirements/guidance of the program and the relevant technical expertise in the area. The closure plan advisory review system illustrates this combination of policy and technical information within a single system. To deviate from this practice and include technical expertise contrary to that contained in regulations or official guidance documents would in effect provide approval for deviation from the regulations or official guidance. The effect of limiting advice to that authorized by the regulatory program may reduce the utility of the systems to decision makers. This situation is illustrated by the final cover advisory system. Final cover designs are commonly proposed which differ from the prescribed RCRA cap but, according to the applicant, have similar operating characteristics. Permit reviewers have requested that the expert system assist in reviewing these designs. The system, however, does not provide advice concerning alternatives to the RCRA cap. This restriction (to a RCRA cap) has reduced the value of the expert system to some permit reviewers. In spite of the potential loss of utility of the systems they can not be supported by the Agency if they provide advice that differs from regulations or official guidance.

CONCLUSION

Expert systems have the potential for providing advice concerning high priority issues that must be evaluated by numerous decision makers within the Agency and the states with regulatory authority.

In order to expedite completion of the systems, the development process for the systems was serial rather than parallel. Hence the systems are not all at same stage of completion. The current contract effort will see the first system, final cover, to completion, i.e., field tested on a limited scale and ready for extensive testing by the targeted user community. The second system, vegetative cover, will be completed through the stage of field testing prototype. The third system, leachate collection, will be completed through demonstration prototype. The fourth and final system, run-on/off will not be completed at this time. Completion of these systems waits a reevaluation of needs in relation to other priorities and availability of resources. Hopefully these systems can all be fully field tested within the next calendar year. Until this is completed and a user support and systems maintenance function are established, the systems will not be ready for general release or use.

DEVELOPMENT OF A NOVEL SUPPORT AERATED BIOFILM REACTOR FOR THE BIODEGRADATION OF TOXIC ORGANIC COMPOUNDS

by: Sandra Woods[1], Kenneth Williamson[1], Stuart Strand[2], Kelly Ryan[1], Jonathan Polonsky[1], Roger Ely[1], Kurt Gardner[1] and Philippe Defarges[1]

[1] Department of Civil Engineering
Oregon State University
Corvallis, Oregon 97331

[2] College of Forest Resources
University of Washington
Seattle, Washington 98195

ABSTRACT

The objective of this project is to develop a biofilm process that successfully degrades hazardous wastes. This is accomplished through the selection of microorganisms by supplying appropriate gases directly to a biofilm supported on a gas-permeable membrane. A gas-permeable membrane has been used successfully as a support surface for the growth of bacterial films in laboratory reactors in two applications: (1) an enrichment culture of methane-oxidizing bacteria and (2) an enrichment consortium of aerobic and anaerobic bacteria.

Methane oxidizing bacteria are enriched on the gas-permeable membrane by providing methane and oxygen to the base of the biofilm. The biofilm degrades the following chlorinated one- and two- carbon compounds in order of decreasing removal rates: dichloromethane, chloroform, 1,2-dichloroethane and cis 1,2-dichloroethene.

For the anaerobic/aerobic consortium, the reactor is operated to enrich for anaerobic microorganisms in the biofilm towards the bulk liquid by maintaining an anaerobic bulk liquid, and aerobes toward the surface of the membrane by providing pure oxygen through the membrane support. The anaerobic portion of the biofilm should facilitate reductive dehalogenation of haloaromatic compounds, and the aerobic portion of the biofilm should allow degradation of the dehalogenated metabolic products. This reactor configuration has been used to successfully treat chlorophenols and chloronitrobenzenes and is being evaluated for the treatment of chlorobiphenyls, chlorobiphenylols, and chlorobenzenes.

INTRODUCTION

A biofilm reactor has been developed that may increase the potential for biodegradation of a wide variety of trace toxicants by facilitating the growth of specific enrichment cultures. The gas-permeable-membrane-supported (GPMS) reactor differs from traditional biofilm processes in that electron donors and/or acceptors are provided to the microorganisms by diffusion of gases through a gas-permeable membrane. In addition to supplying substrates directly to the biofilm, the membrane also physically supports the biofilm and the overlying bulk liquid.

The treatment of low-molecular-weight chlorinated solvents by an enrichment culture of methylotrophic bacteria and the treatment of chlorinated aromatic compounds by an aerobic/anaerobic consortium are described in this paper. The objective of this project was to determine the feasibility of the GPMS reactor for the treatment of a variety of hazardous compounds through the selection of appropriate groups of microorganisms. The reactor was fed synthetic wastewaters containing the following trace toxicants: chlorophenols, chlorinated nitrobenzenes, polychlorinated biphenyls, methylene chloride, chloroform, carbon tetrachloride, 1,2-dichloroethane and cis 1,2-dichloroethene.

In one reactor, methane oxidizing bacteria were selected for study due to their ability to degrade a wide range of organic compounds. Methylotrophs use single carbon compounds as electron donors and carbon sources with oxygen serving as the electron acceptor. They oxidize methane to carbon dioxide through the use of several enzymes in a series of reactions involving sequential transfers of two electrons. The initial oxidation of methane to methanol is catalyzed by the methane monooxygenase enzyme (MMO). Methanol is further oxidized to form formaldehyde, formic acid and CO_2. The methane monooxygenase enzyme is thought to be largely responsible for the broad degradative competence of methylotrophs (1).

The methylotrophic biofilm was developed by providing methane and oxygen through the membrane. Because methane and oxygen are sparingly soluble gases, the growth of methylotrophs was facilitated in the GPMS reactor by providing methane and oxygen directly to the microorganisms through the membrane.

In another reactor, an anaerobic/aerobic consortium was developed to encourage the biodegradation of haloaromatic compounds. These compounds are biodegraded by different mechanisms in aerobic and anaerobic pathways. Under aerobic conditions, many chlorophenols, chlorobenzoates and chlorobiphenyls are degraded by hydroxylation followed by cleavage of the aromatic ring. Chlorines are removed from the compound after the ring is cleaved (2). In contrast, a very different degradative pathway exists under anaerobic conditions. Chlorophenols (3,4) chlorobenzoates (5), and polychlorinated biphenyls (6) are reductively dehalogenated under anaerobic conditions. In the GPMS reactor, the dechlorinating ability of anaerobic consortia and the ability of aerobic consortia to hydroxylate and cleave the ring are both present and potentially increase the biodegradation of these compounds as the metabolic products are exchanged between the two bacterial groups by diffusion.

An aerobic/anaerobic biofilm was developed by providing oxygen at the base of the biofilm to encourage the growth of aerobic organisms and by providing high concentrations of electron donors to develop anaerobic conditions in the bulk liquid. The reactor was fed chlorinated aromatic compounds in a nutrient media consisting of inorganic minerals, vitamins and carbon sources.

EXPERIMENTAL METHODS AND ANALYTICAL PROCEDURES

Several independent studies were conducted (Table 1). In each study, the biofilm reactor was altered as experience was gained in operation. The reactor design, nutrient solution and analytical methods for each individual study is described in the listed references.

TABLE 1. GPMS BIOFILM STUDIES

Compounds	Reference
Methylotrophic Consortium	
chlorinated methanes	7,8
dichloromethane, 1,2-dichloroethane and cis 1,2-dichloroethene	8,9
halo -methanes, -ethanes, and -ethenes	in progress
Aerobic/Anaerobic Consortium	
chlorophenols	10
chlorinated nitrobenzenes	11,12
polychlorinated biphenyls	13
chloroaromatic compounds	in progress

SYSTEM DESIGN

A schematic diagram of the GPMS reactor system used to treat chlorinated low-molecular-weight solvents is shown in Figure 1 (8). Methylotrophs were enriched by providing a 50/50 volume/volume mixture of methane and oxygen through the membrane. The aerobic/anaerobic consortium was enriched by providing pure oxygen through the membrane.

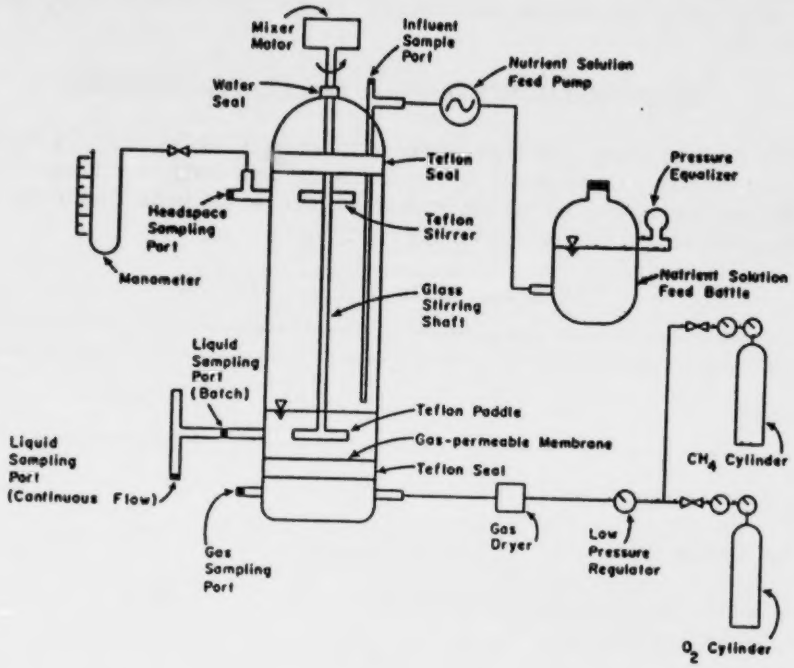

Mixer Motor
Influent Sample Port
Nutrient Solution Feed Pump
Water Seal
Teflon Seal
Pressure Equalizer
Headspace Sampling Port
Teflon Stirrer
Manometer
Nutrient Solution Feed Bottle
Glass Stirring Shaft
Liquid Sampling Port (Batch)
Teflon Paddle
Gas-permeable Membrane
CH_4 Cylinder
Teflon Seal
Liquid Sampling Port (Continuous Flow)
Gas Dryer
Low Pressure Regulator
Gas Sampling Port
O_2 Cylinder

Figure 1. Reactor Schematic for the Growth of Methylotrophs

The reactor was constructed of standard 4-inch ID glass beaded process pipe. Glass ports for the addition and removal of nutrient solution and gaseous substrates, and for sampling the headspace and gas compartments were added as shown. The reactor was built in three sections which were connected by flanged joints sealed with Teflon gaskets. The gas-permeable membrane was installed across the flanged joint between the gas and liquid compartments. The membrane material selected after evaluation of several materials was a nylon-backed Teflon laminate manufactured by W.L. Gore and Associates (Elkton, Maryland) and commonly called Goretex. The reactors were held in a 30°C incubator.

Gases were provided to the biofilm through the ports in the gas compartment. A low pressure regulator was used by Ryan (9) and Polonsky (13) to maintain a constant pressure of approximately five inches of water in the gas compartment. Gas consumption was monitored by measuring pressure loss in the gas storage tanks. In studies by Ely (7,8) and Gardner (11) a small gas flow rate was maintained through the gas compartment.

NUTRIENT MEDIA

The nutrient media for the growth of methylotrophs was a variation of the nitrate mineral salts media described by Whittenbury et al. (14). It is a defined media containing inorganic nutrients and EDTA. Nitrate serves as the nitrogen source.

The nutrient feed solution for the aerobic/anaerobic consortia consisted of mineral salts, trace elements, vitamins and carbon sources necessary to sustain aerobic and anaerobic bacterial growth. The solution used to treat polychlorinated biphenyls (13) and chlorinated nitrobenzenes (11) were developed based on a modification of the nutrient media described by Owen et al. (15). Glucose, methanol, acetic acid and acetone were provided as alternate carbon sources to generate anaerobic conditions in the bulk liquid.

ANALYTICAL METHODS

Methane, oxygen, nitrogen, and carbon dioxide were measured using a Fisher Model 25V gas partitioner with two columns, one containing 30% bis (2-ethoxyethyl) adipate (BEEA) on 60/80 Chromosorb PAW and the other containing 45/60 Molecular Sieve 13X (Supelco, Inc., Bellefonte, Pennsylvania). Gas samples (100 uL) were collected using a Pressure-Lok, gas-tight syringe and immediately injected into the gas partitioner for analysis. Standards curves were prepared daily.

Concentrations of the chlorinated compounds were determined using a Hewlett-Packard Model 5890A gas chromatograph equipped with a Hewlett-Packard Model 3392A integrator. Chloromethanes, chloroethanes and chloroethenes were determined by direct injection of liquid or gas samples and gas chromatography with flame ionization detection. A 1/4-inch glass column, 8 feet in length and packed with 60/80 Carbopack B with 1% SP-1000, was used for the separation.

Chlorinated aromatic compounds were measured with splitless injection of hexane extracts and gas chromatography with electron capture detection. A 30 m x 0.33 mm DB-5 with at 0.25 um film thickness fused silica capillary column (J&W Scientific, Deerfield, IL) was used to separate PCBs. A DB-1 fused silica capillary column (J&W Scientific, Deerfield, IL) was used for the separation of chlorophenols and chlorinated nitrobenzenes.

RESULTS AND DISCUSSION

METHYLOTROPIC CONSORTIUM

The original bacterial inocula for the selection of methylotrophic bacteria consisted of 10 ml of thickened trickling filter effluent from the Corvallis, Oregon municipal wastewater treatment plant and 10 ml of thickened sludge from a bench-scale anaerobic digester in operation at the Oregon State University Environmental Engineering Laboratory. The culture was enriched for methylotrophs by providing methane as the principal carbon source and by maintaining a moderate flow of nutrient solution (without carbon sources) to wash out undesired organisms.

Once the biofilm was established, the reactor was fed a group of chlorinated low-molecular-weight compounds in a series of experiments. Mass balances were performed for each of the chlorinated compounds throughout the experiments by measuring concentrations of the compounds in the reactor influent, liquid phase, headspace and gas compartment.

The removal of dichloromethane, chloroform, and carbon tetrachloride was evaluated in a batch test. A total mass of 20.6 umol dichloromethane, 19.6 umol chloroform, and 42.7 umol carbon tetrachloride were added together to yield initial liquid phase concentrations of 10.9 umol/l dichloromethane, 9.88 umol/l chloroform, and 19.59 umol/l carbon tetrachloride. The liquid phase concentrations of each compound decreased rapidly. After seven days (168 hours), the concentration of dichloromethane in the liquid phase was below detection; the liquid concentration of chloroform fell to less than 3.2 umol/l; and the liquid concentration of carbon tetrachloride fell to 4.6 umol/l.

The mass balance for dichloromethane is shown in Figure 2. The total loss of dichloromethane was 16.2 umol of which 4.4 umol escaped through the membrane in the small gas flow through the gas compartment. Although an initial increase in the mass of dichloromethane in the headspace was observed, this mass eventually fell to near zero. This was due to an initial equilibration of the headspace with the bulk liquid, and reequilibration as the dichloromethane present in the bulk liquid was biodegraded. Based on these data, 16.2 umol of dichloromethane was removed.

Chloroform also was removed during this experiment; however, removal rates were much slower than the rate for dichloromethane. After seven days, 6.0 umol chloroform of the 19.6 umol initial mass remained in the reactor of which 10.3 umol left the reactor through the membrane and gas compartment (Figure 3). Based on these data, a maximum of 3.3 umol may have been biodegraded.

Carbon tetrachloride data were similar to data for chloroform. Of the initial mass of 42.7 umol added to the reactor, 17.5 umol remained in the reactor after seven days; 16.3 umol left the reactor through the membrane and gas compartment. Based on these data, a maximum of 8.9 umol carbon tetrachloride was removed during this test. The initial removal of 8.9 umol was probably largely due to sorption since the mass decreased quickly within the first three days and then remained constant.

In a second series of tests with the methylotrophic biofilm (8,9), the removal of dichloromethane (DCM), dichloroethane (DCA) and cis 1,2-dichloroethene (DCE) was evaluated. The masses of the chlorinated compounds in each compartment (liquid, headspace and gas compartment) are presented in Figures 4, 5 and 6. Immediate substantial decreases in the masses of chlorinated compounds in the liquid were observed in all cases with a corresponding increase in the masses of compounds in the gas and headspace. This initial transfer resulted from the volatilization of these compounds. A small fraction of the masses was unaccounted for and is likely to be sorbed to the biofilm and reactor vessel.

A control study was conducted by adding dichloromethane (DCM), dichloroethane (DCA), and cis 1,2-dichloroethene (DCE) without the presence

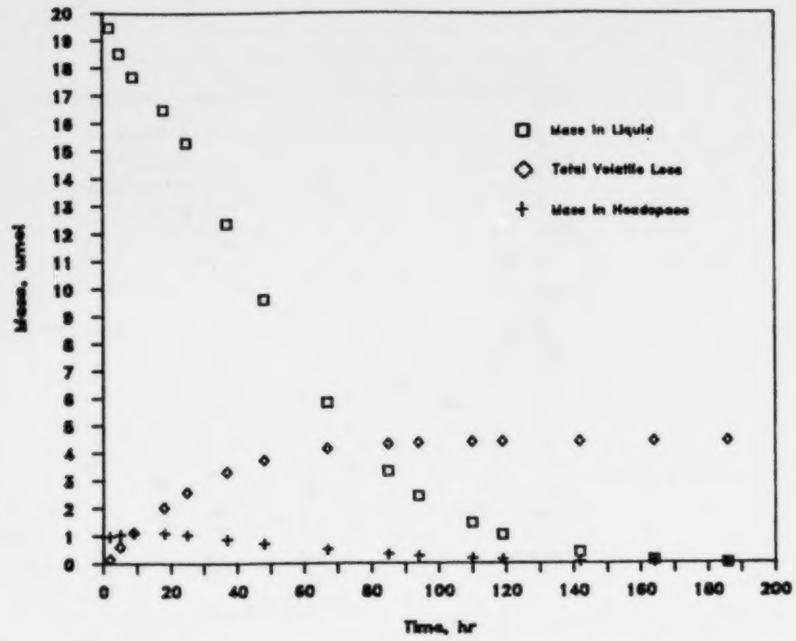


Figure 2. Dichloromethane Mass Balance

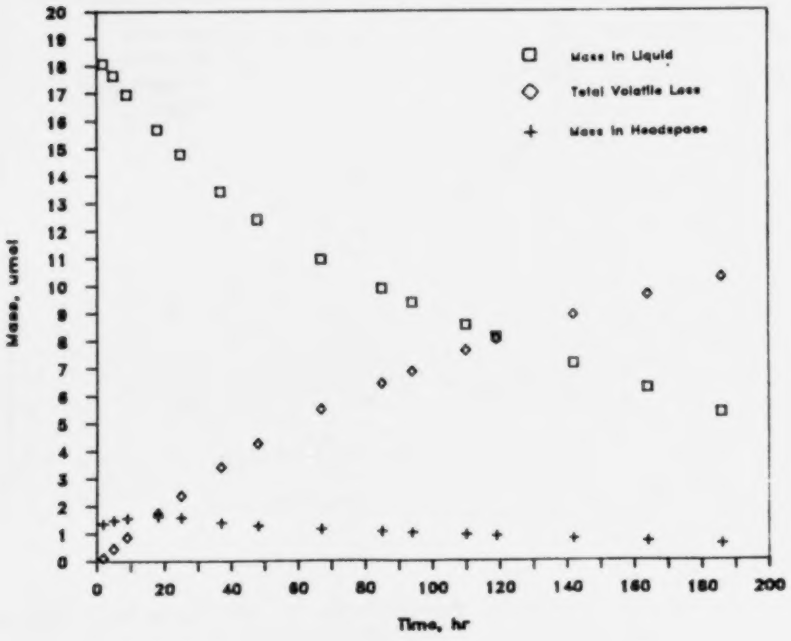


Figure 3. Chloroform Mass Balance

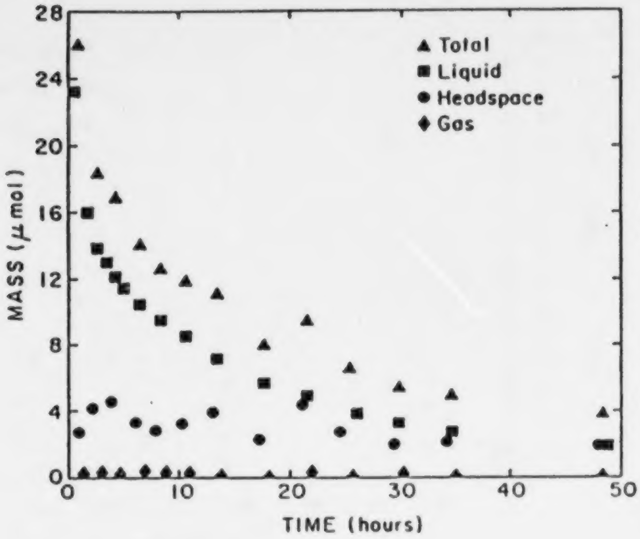


Figure 4. Mass Balance for the Batch Degradation of Dichloromethane

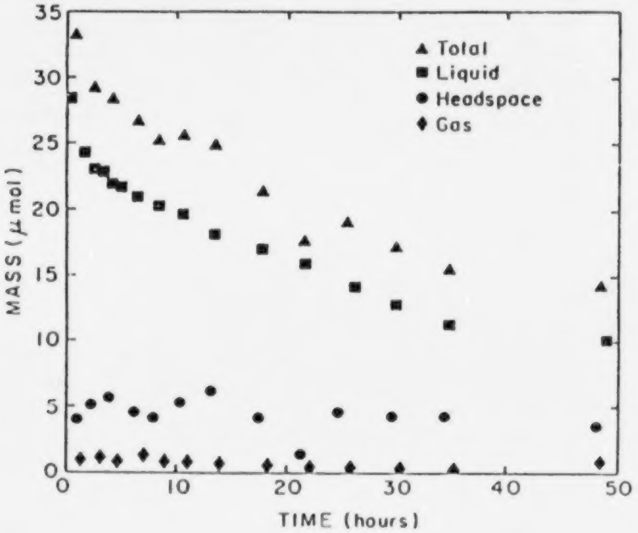


Figure 5. Mass Balance for the Batch Degradation of 1,2-Dichloroethane

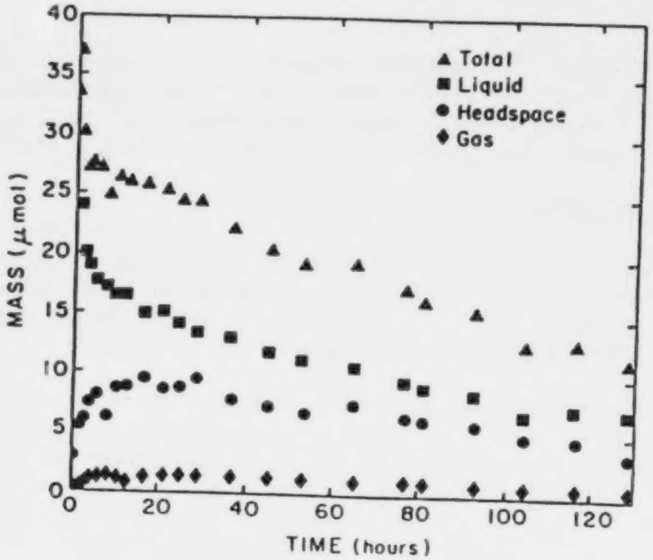


Figure 6. Mass Balance for the Batch Degradation of cis 1,2-Dichloroethene

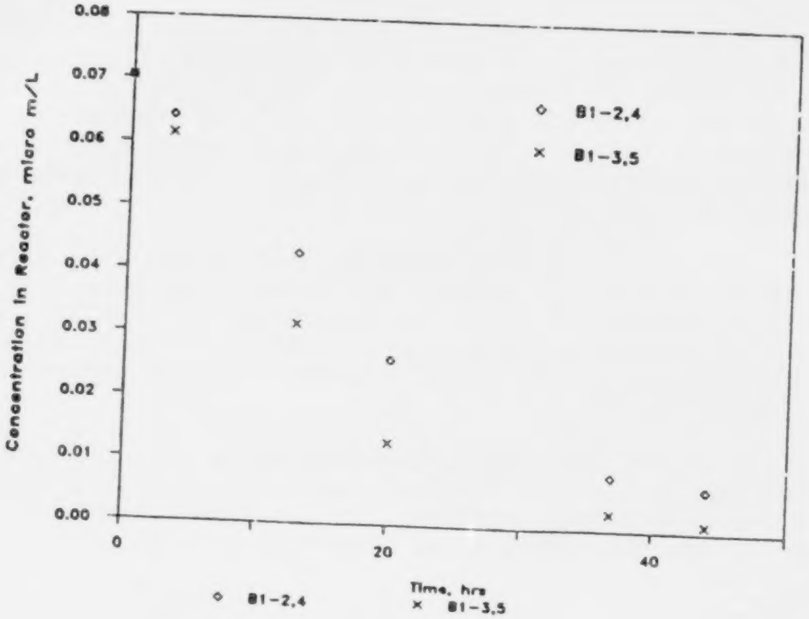


Figure 7. Liquid Phase Dichloronitrobenzene Concentrations During Batch Biodegradation

of the biofilm. The concentrations of the compounds were monitored over a 40-hr period and no significant loss of the chlorinated compounds was measured. These results showed the absence of significant abiotic removal mechanism such as hydrolysis or adsorption to the reactor.

AEROBIC/ANAEROBIC CONSORTIUM

Similar reactors were operated with oxygen supplied at the base of the Goretex support. These reactors were operated at moderately high organic loading rates to generate an anaerobic bulk liquid and a thick biofilm; an aerobic zone existed at the base of the biofilm.

Dichloronitrobenzene (DCNB) removal was evaluated in a series of batch and continuous flow experiments (11). Two dichloronitrobenzenes (2,4-DCNB and 3,5-DCNB) were tested to evaluate the effect of chlorine position on removal. The concentration of both compounds in the reactor liquid rapidly decreased (Figure 7). The ortho-para substituted dichloronitrobenzene was removed slightly faster than the meta-meta substituted compound. No metabolic products appeared in the batch reactor during this experiment. However, subsequent continuous flow experiments indicated the presence of chlorinated anilines which result from reduction of the nitrate functional group to an amine.

SUMMARY AND CONCLUSIONS

A variety of chlorinated compounds were successfully biodegraded in with a gas-permeable membrane-supported biofilm under two applications: (1) an enrichment for methane-oxidizing bacteria and (2) an enrichment consortium of aerobic and anaerobic bacteria. By controlling the type of gas transferred through the gas-permeable membrane, the electron donors and electron acceptors and bacterial consorium was successfully selected for the compounds to be removed.

A biofilm of methane oxidizing bacteria was grown on the gas-permeable membrane by providing methane and oxygen to the base of the biofilm. The biofilm degraded the following chlorinated one- and two- carbon compounds in order of decreasing removal rates: dichloromethane, chloroform, 1,2-dichloroethane and cis 1,2-dichloroethene. Carbon tetrachloride was not biodegraded.

A biofilm comprised of anaerobic and aerobic layers was developed by providing high organic substrate levels in the liquid compartment and oxygen to the gas-permeable membrane. The anaerobic/aerobic biofilm successfully biodegraded chlorophenols and chloronitrobenzenes.

REFERENCES

1. Higgins, I., Best, D., and Hammond, R. New findings in methane-utilizing bacteria highlight their importance in the biosphere and their commercial potential. Nature, 286: 561, 1980.

2. Hartmann, J., Reineke, Wl, Knackmuss, H.J. Metabolism of 3-chloro-, 4-chloro-, and 3,5-dichlorobenzoate by a Pseudomonad. Applied and Environmental Microbiology, 37: 421, 1979.

3. Woods, S. The fate of chlorinated, hydroxylated and methoxylated benzenes in anaerobic wastewater treatment. Dissertation, University of Washington, Environmental Engineering and Sciences, Seattle, Washington, 1985. 301 pp.

4. Boyd, S. and Shelton, D. Anaerobic biodegradation of chlorophenols in fresh and acclimated sludge. Applied and Environmental Microbiology 47: 272, 1984.

5. Suflita, J., Horowitz, A., Shelton, D., and Tiedje, J. Dehalogenation: a novel pathway for the anaerobic biodegradation of haloaromatic compounds. Science 218: 1115, 1982.

6. Low, E. and Woods, S. Reductive dechlorination of chlorobiphenyls during anaerobic treatment. Submitted to Environmental Science and Technology, 1988.

7. Ely, R. Startup and performance of a gas-permeable-membrane-supported (GPMS) biofilm system using a mixed culture of methylotrophs to degrade methylene chloride, chloroform, and carbon tetrachloride. Thesis, Department of Civil Engineering, Oregon State University, Corvallis, Oregon, 1986.

8. Ely, R., Ryan, K., Woods, S., Williamson, K., and Strand, S. Treatment of chlorinated one- and two- carbon compounds by methylotrophs using a gas-permeable-membrane-supported-biofilm reactor. In preparation, 1988.

9. Ryan, K. Development of a method to elucidate biodegradation pathways of chlorinated one- and two- carbon compounds using a gas-permeable-membrane-supported methylotrophic biofilm. Thesis, Oregon State University, Department of Civil Engineering, Corvallis, Oregon, 1988.

10. Defarges, P. Development of a submerged aerated biofilm process for the degradation of chlorophenols. Thesis, Oregon State University, Corvallis, Oregon, 1987.

11. Gardner, K. Development of a method to accumulate metabolic products from dichloronitrobenzenes using a gas-permeable-membrane-supported biofilm. Thesis, Oregon State University, Department of Civil Engineering, Corvallis, Oregon, 1987.

12. Woods, S., Ryan, K., and Gardner, K. Development of a method to accumulate metabolic products. In preparation, 1988.

13. Polonsky, J. Development of a gas-permeable-membrane-supported biofilm reactor for the combined aerobic/anaerobic treatment of chlorinated biphenyls. Thesis, Oregon State University, Department of Civil Engineering, Corvallis, Oregon, 1988.

14. Whittenbury, R., Phillips, K., and Wilkinson, J. Enrichment, isolation, and some properties of methane-utilizing bacteria. J. Gen. Microbiol., 61: 205, 1970.

15. Owen, W., Stuckey, D., Healy, J., Young, L., and McCarty, P. Bioassay for monitoring biochemical methane potential and anaerobic toxicity. Water Research, 13: 485, 1979.

MICROBIAL MINERALIZATION OF ORGANIC CONTAMINANTS ON SOILS AND SOIL FRACTIONS

D.S. Kosson, W.V. Black and R.C. Ahlert
Rutgers, The State University of New Jersey
Department of Chemical and Biochemical Engineering
P.O. Box 909
Piscataway, NJ 08855-0909

ABSTRACT

The focus of this paper is preliminary evaluation of biodegradation of organic contaminants on excavated soils and separated soil fines using activated sludge populations in slurry reactor configurations. Contaminated soils display a wide variety of sorbed and chemically bound organic species; generally, only a limited number are present in high concentrations. Priority pollutants usually represent only a small percentage of total leachable or extractable contaminants capable of impacts on public health and environmental quality. Given the diversity of contaminants present, serial microbial processing, controlled to maximize the rate of individual degradation steps is being investigated. Several soil samples have been obtained from locations at a CERCLA-NPL site immediately adjacent to an impoundment used for disposal of distillation bottoms from a benzene, toluene and xylene (BTX) production process.

INTRODUCTION

An increasing number of dump and disposal areas for hazardous and toxic substances have been identified. Within reasonable time, these sites must be renovated and their potential for impacts on public health and the environment mitigated completely. In typical circumstances, one or more waste materials have been buried or discharged with little or no provision for long-term containment. Many dump sites have received wastes from several sources and, as a direct consequence, the contaminant matrix is extremely complex and includes organic species, heavy metals, inorganic salts and oxides, and/or inert materials under strongly acidic, basic, oxidizing or reducing conditions.

The current physical and chemical state of a waste may not reflect the initial state. The original states of abandoned wastes include hydrophilic and hydrophobic liquids, gels, sludges, powders, dispersions of particulates and/or liquids, emulsions, tarry or viscous materials, sorbed chemicals and agglomerates. The current state is a result of a site- specific scenario that could involve container failure, chemical reactions between wastes, weathering (natural or enhanced acidic rainfall, oxidation, etc.), aerobic/anaerobic microbial degradation, and interactions with soil and water.

Once a waste disposal site has been identified, a series of actions must be carried out to establish the chemical, physical, and biochemical character of the contamination, the distribution and extent of dispersal of contaminants, and the potential for rapid migration by diffusion or gross movement via air or water. After the scope of the problem has been outlined, a plan for containment, stabilization, clean-up and ultimate destruction or permanent (reversible) isolation of recovered waste, or waste by-products, can be developed.

Transfer off-site for complete destruction of wastes or decontamination of soils is one available option. High-temperature processing and oxidation, e.g., incineration, ozone, wet air oxidation, etc., have been demonstrated. Disadvantages include high unit cost, high capital cost, high containment and hauling costs, problems associated with gaseous and solid residuals disposal and mechanical problems relating to handling large quantities of inert material (soil).

On-site management of hazardous wastes avoids many transfer-related problems. Personnel and environmental exposures during handling, packaging and transportation are minimized and localized. Responses to leaks, spills, equipment failures, gaseous emissions and other fortuitous events can be rapid and comprehensive. In short, contamination can often be confined to an area already judged to be contaminated; personnel protection and training can be consistent with the requirements of site activities. Physical, chemical, and biological treatment methodologies can be made available at most sites. The goal of treatment may be waste destruction, detoxification or stabilization for long-term, local storage. In many instances extraction of water and excavation of soil for treatment, as opposed to in-situ treatment, will achieve better control, accountability and effluent quality assurance. Many believe the ideal solution is permanent, on-site destruction.

APPROACH

Microbial degradation with activated sludge inocula has been used with great success for total mineralization of organic residues. In particular, an array of high-strength, hazardous, organic solutes in aqueous systems has been destroyed by aerobic, anaerobic or a combination of aerobic and anaerobic bioreaction steps. The distribution of organic contaminants between soil and water is specific to molecular type, soil characteristics, water content, pH and oxygen tension. Factors of concern include:

i. Simple sorption equilibria with single solutes and soil constituents acting independently.

ii. Competitive sorption of organic solutes on individual or interacting soil fractions.

iii. Chemical reactions with natural organic matter, i.e., hydrogen-bonding, esterification, etc.

iv. Slow anaerobic fermentation with fatty acid production, low pH, and highly reducing conditions.

v. Entrapment in clay mineral structures, such as irreversible clathyration and catalytic conversion by specific clay mineral ions or crystal configurations.

vi. Physical immobilization of contaminant molecules in small pores and capillaries by dewatering, surface tension effects, or restricted diffusion paths.

Treatment strategy is dictated in large measure by the combination of those contaminant/soil/water interactions that influence behavior at a site. Four general behavior patterns, or "Cases", can be cited to illustrate the options:

Case I: **Readily reversible sorption equilibria and partition coefficients that favor groundwater and soil water.**

Case II: Reversible sorption and/or reaction with kinetic, diffusion rate limitations, or unfavorable partitioning.

Case III: Irreversible chemisorption, chemical binding, and physical trapping.

Case IV: Immiscible organic phase stabilization by surface tension (capillary) effects.

A number of process steps can be combined into a complete scheme for separation and elimination of polluting organic species. Given a range of natural organic fractions and clay mineral species in soils, the organic contaminants can be anticipated to include normally volatile priority pollutants, solvents, PCDDs and PCDFs, PCBs, pesticides, PNAs and PAHs, and poorly defined complex solutions from manufacturing and blending operations. Much effort has been expended to define the efficiencies, costs, limitations, and final quantitative outputs from individual operations and some combinations of operations. The major exception is biological treatment of contaminated soil; this technology is virtually unexplored.

The goal of this study is to characterize the cost effectiveness and biochemical efficiency of microbial treatment for leachates and fine fractions of excavated soil. Contaminants that occur at various actual hazardous waste disposal sites and can be expected to reflect a diversity of organic compounds, including many that are nominally xenobiotic.

A treatment process for surficial soils will employ excavation, component separation, chemical pretreatment, sequenced microbial degradation processes, soil reconstitution, and soil replacement. Soil excavation permits greater process control and variety of process conditions than in-situ treatment. Soil component separation is an attractive process step. Often a major portion of the contaminants are present on a particular soil fraction, for example, contaminant binding to a soil may be dictated by solute adsorption to the clay mineral fraction or by partitioning with the natural organic (humic) fraction.

In many cases, acceptable remedial efficiency may be achieved through special treatment of the small, quantities of highly contaminated soil fines that are obtained through dry fractionation. Alternately, the fine fraction may be generated as a slurry in a wash or extraction solution formulated with surfactive agents and/or chemicals to redistribute sorbed contaminants. The focus of the project is development of a series of microbial reactors for treatment of soil fines (containing clay and humic fractions) and slurries of fines in leachate or extraction solutions.

Contaminated soil will display a wide variety of organic contaminants with a limited number of species present in high concentrations. In general, the sum of priority pollutants present represents only a small percentage of total leachable or extractable contaminants. Thus, key species and gross parameters (i.e., COD, TOC, etc.) are usually employed as indicators of treatment effectiveness. Given the diversity of contaminants potentially present, a series of microbial processes using activated sludge inocula in separate reaction vessels, controlled to maximize the rate of individual degradation steps at particular conditions, is a promising treatment technology. Specific organic species have been shown to be biodegraded through multiple pathways. There is no intent to use genetically engineered or specially cultured microorganisms or enzymes derived therefrom.

Specific sequences of aerobic and anaerobic treatment steps should be based on (i) the nature and diversity of contaminants present, (ii) the type of soil/contaminant binding, and (iii) regulatory expectations. Use of enriched oxygen supplies or elevated temperatures and pressures should also by included. An additional process variable is moisture content. Moisture content may be adjusted to enhance microbial processes or to facilitate materials handling. Most treatment steps will require modification of nutrient levels and pH corrections to accommodate the microorganisms used.

The technical organization of the project is a phased approach. Phase One consists of the identification of a suitable matrix of soil types, contaminant-soil binding types, and organic contaminant mixtures. This matrix represents soil contamination occurrences at CERCLA-NPL sites. Phase Two of the project is devoted to the investigation of the effectiveness of microbial process steps. Batch and continuous reactors will be operated to evaluate competitive effects resulting from mixed organic species on microbial processes. This phase is oriented toward the development and evaluation of process sequences. Pretreatment steps may include separations of soil fractions and chemical reactions, such as oxidation or hydrolysis, to selectively transform refractory organic compounds into intermediates more amenable to biodegradation. Later Phases of the activity will address overall process selection criteria, complete process demonstrations, and scale-up procedures for prototype applications.

SITE DESCRIPTION

Soil samples were obtained from areas immediately adjacent to a section of a CERCLA-NPL site where distillation bottoms from a BTX production facility were impounded. The lagoon is in excess of ten acres in size and contains more than 100,000 yd^3 of impounded material. The lagoon contents have separated into several layers including, from lagoon bottom to surface, a solid mixed organic/inorganic layer, tar-like layer, viscous liquid organic layer, and floating aqueous layer. Migration of lagoon contents to neighboring soils has occurred.

Properties of the soils sampled are provided in Table 1. In addition, the presence of polynuclear aromatic species (PNAs) was determined semi-quantitatively using high pressure liquid chromatography (HPLC) techniques. Ten gram soil samples were serially extracted three times with 80 mL cyclohexane. Extraction was achieved through mixing with a sonic disrupter for three minutes followed by solids separation and re-extraction. Serial extracts were combined and quantitatively concentrated to a total volume of 240 mL. A typical extract chromatogram and a PNA locator standard are provided in Figures 1a and 1b. A summary of identified species and order-of-magnitude quantification is provided in Table 2; numerous unidentified species are present.

BIODEGRADATION IN SLURRY REACTORS

Initial studies have been focused on using an activated sludge inoculum dispersed with bulk soil samples in an aqueous nutrient media. Activated sludge samples were obtained from the Somerset-Raritan Sewage Treatment Authority, a secondary treatment facility that receives significant inflow fraction from industrial wastewater. The intent of these studies has been to establish a baseline for comparison of alternative microbial processes and reactor configurations. Sucrose was employed as a co-substrate to avoid substrate-limiting initial conditions. The reactor was operated in a batch mode. These conditions were considered to be the simplest meaningful configuration.

TABLE I

PROPERTIES OF SOIL SAMPLES

Property	Sample 1-S	Sample 1-E
pH:	3.6	3.5
Texture (%):		
Sand	66	70
Silt	26	20
Clay	8	10
Cation Exchange Capacity (meq/gm):	6.6	5.7
Principle Exchangeable Cations: (meq/100gm)		
Ca	0.04	0.17
Mg	0.10	0.30
K	0.004	0.05
Na	0.15	0.07

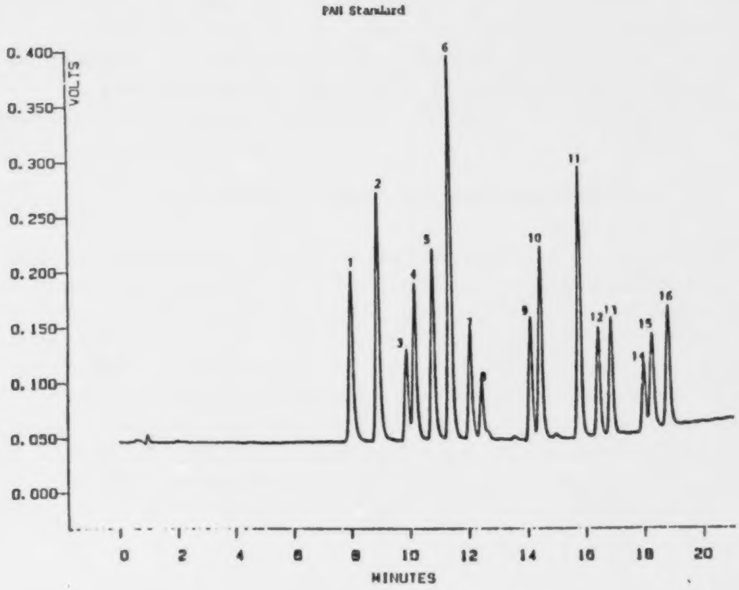


Figure 1a

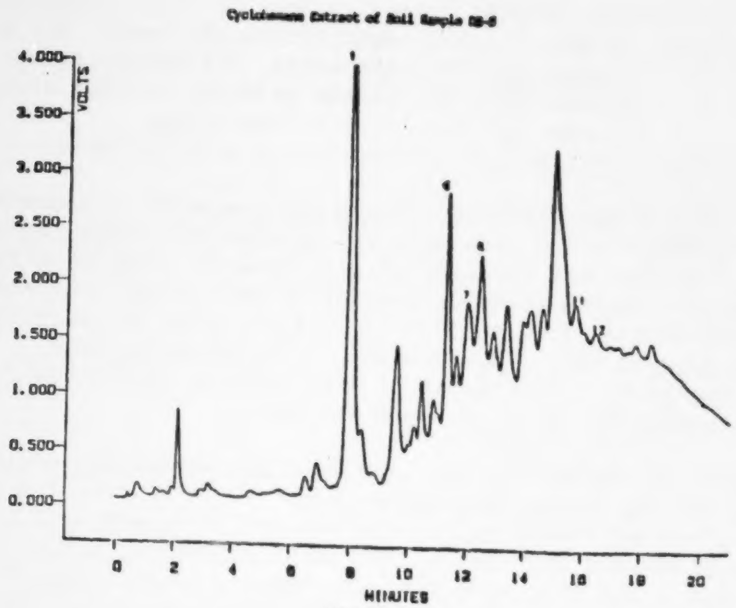


Figure 1b

TABLE 2

Semi-Quantitative Soil Assays For PNAs

Peak	Time (Min)	Component	Locator Mix (mg/L)	Concentration (mg/kg) 1-N	1-S (Fig. 1b)	1-E
1	7.97	Napthalene	10	5100	90	40
2	8.87	Acenaphthylene	20	-	-	-
3	9.87	Acenaphthene	10	-	-	-
4	10.14	Fluorene	2	-	-	-
5	10.76	Phenanthrene	1	-	-	-
6	11.34	Anthracene	1	80	2	1
7	12.04	Fluoranthene	2	700	-	8
8	12.44	Pyrene	1	600	6	3
9	14.11	Benzo(A)anthracene	1	-	4	1
10	14.45	Chrysene	1	-	-	-
11	15.81	Benzo(b)fluoranthene	2	-	-	7
12	16.49	Benzo(k)fluoranthene	1	-	-	-
13	16.93	Benzo(a)pyrene	1	-	-	-
14	18.04	Dibenzo(a,h)anthracene	2	-	-	-
15	18.31	Benzo(g,h,i)perylene	2	-	-	-
16	18.86	Indeno(1,2,3-c,d)pyrene	1	32	6	1

HPLC Column: Supelcosil LC-PAH; 15cm X 4.6mm, 5 micron packing
Solvent Flow: 8 min. 2mL/min. equilibrate 65% water, 35% acetonitrile:
2 min. 2mL/min. 65% water, 35% acetonitrile;
14 min. 2mL/min. linear gradient to 100% acetonitrile
5 min. 2mL/min. 100% acetonitrile

Typical process operating conditions and responses are described as follows. Initially, a 5-L fermentor was charged with 500g of soil, 14g of sucrose, nutrients and 3.5 L of distilled water. The resulting dissolved organic carbon (TOC) concentration was 1900mg C/L, comprised of 1680 mg C/L derived from sucrose (SOC) and 110 mg C/L resulting from sorptive equilibrium with dispersed soil. The aeration rate, temperature and pH were maintained at 4 L(STP)/min, 30°C, and 7.0-7.1, respectively using automated feedback controls.

Carbon dioxide evolution, TOC, and acid production was monitored continuously during reactor operation (Figs. 2-4). Subsequent to an initial lag phase of 5 hrs, carbon dioxide evolution and acid production (predominately sucrose conversion) increased rapidly to peak production rates at 10 hrs. TOC decreased linearly between hours 5 and 28 at a rate of 210 mg C/hr. The final TOC of 110 mg/L represented 94% TOC and 36% EOC reduction (on a concentration basis).

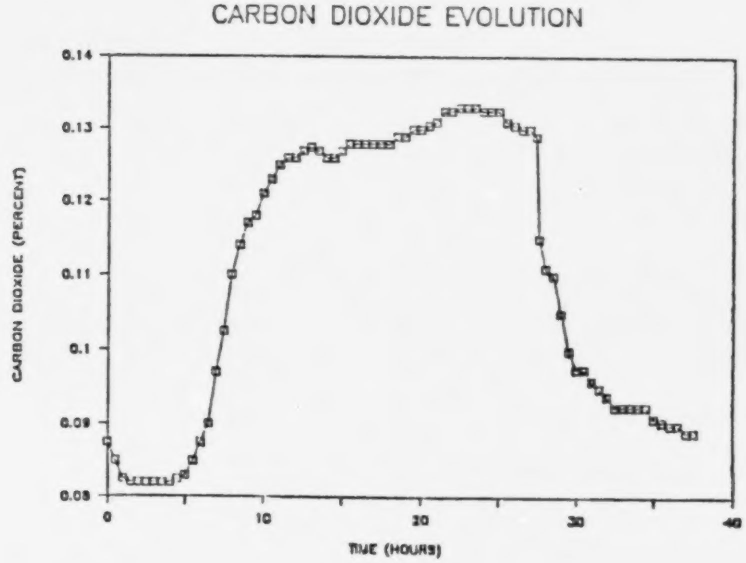


Figure 2

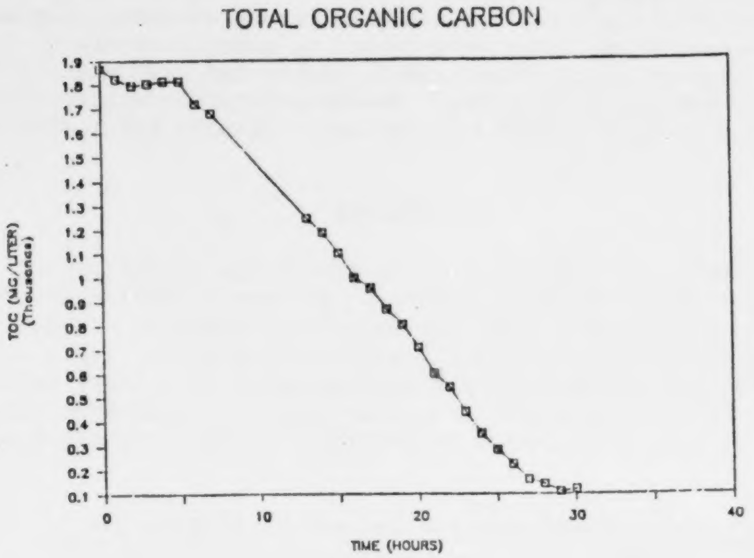


Figure 3

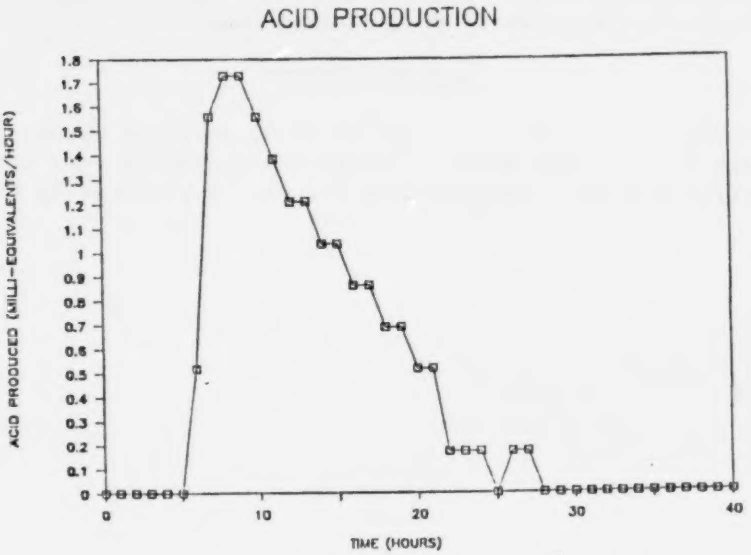


Figure 4

A mass balance on carbon was calculated at the conclusion of each trial. For the typical case presented, 6.1 g C was removed from the aqueous solution. Probable carbon end-states include cell mass production, carbon dioxide evolution and partitioning with dispersed soils. A total of 1.5 g C was converted to carbon dioxide. Currently, analytical procedures are under development to quantitatively differentiate between partitioned organic carbon and cell mass in the dispersed heterogeneous solid phase. Post-fermentation extractions followed by HPLC analysis yielded inconclusive results for indicator PNAs.

CONCLUSIONS

Investigations are in progress to delineate the capability of different activated sludge-based microbial process scenarios and reactor configurations to degrade organic contaminants present in or bound to soils. A fractional factorial matrix with contaminant(s) type, soil type, microbial process, and reactor configuration as primary factors will serve as a basis for comparison. Subsequently, individual process steps will be evaluated in series to provide a basis for overall process evaluation.

Preliminary studies have been carried out to examine the biodegradation of organic species in soils contaminated by BTX distillation bottoms. Results from a slurry reactor with dispersed soil and activated sludge culture will serve as a basis for comparison with alternative microbial (aerobic and anaerobic) process steps. Substantial methods development is necessary for clear evaluation of treatment effects on contaminants in the solid phase.

ACKNOWLEDGEMENT

This work was supported in part by USEPA Cooperative Agreement No. CR-814055. Mention of trade names or commercial products does not constitute endorsement or recommendation for use by USEPA or by Rutgers University.

BIOLOGICAL TREATMENT OF LEACHATE/NEW LYME, OHIO

by: Edward J. Opatken, Hinton K. Howard, James J. Bond
U. S. Environmental Protection Agency
Hazardous Waste Engineering Research Laboratory
Cincinnati, Ohio 45268

ABSTRACT

Studies have been completed on treating a leachate from New Lyme, Ohio. The Leachate was transported to Cincinnati, Ohio, where a pilot-sized rotating biological contactor (RBC) was used for a treatment evaluation.

The biomass was developed on the RBC discs with primary effluent from the City of Cincinnati's Mill Creek Sewage Treatment Facility. Experiments were then conducted to determine the effectiveness of treating a hazardous waste leachate and to provide information on the following:

- The kinetic rate of organics removal;
- The final effluent quality;
- The fate of priority pollutants and specific organic compounds;
- The loss of volatiles via stripping in the RBC.

This paper reports on the results from these experiments and the applicability of an RBC to treat a hazardous waste leachate from a Superfund site.

BACKGROUND

Land disposal of organic wastes is no longer regarded as an ultimate solution for solid wastes because of the potential for leachate formation and/or groundwater contamination. Leachate releases have occurred at waste disposal sites and technology is needed to remedy these conditions.

Biodegradation of the organics in leachates may provide an acceptable and cost effective alternative for treating leachates. The rotating biological contactor (RBC) was selected as a biological treatment process to study its applicability for converting the organics in leachate into innocuous products. A pilot sized unit was installed at the U. S. Environmental Protection Agency's Test and Evaluation Facility (T&E) in Cincinnati, Ohio, to conduct such an investigation.

NEW LYME SUPERFUND SITE

The New Lyme Superfund site (1) was selected as the source for the leachate. New Lyme is located in Ashtabula County, Ohio, approximately 40 kilometers (25 miles) north of the city of Youngstown, Ohio. The site consists of 14 to 16 hectares (35 to 40 acres) of landfill and began its operations in 1969. It operated as a combined municipal and industrial waste landfill where approximately 230,000 cubic meters (300,000 cubic yards) of wastes were disposed of each year. The industrial wastes included paints, solvents, oils, coal tar distallates and corrosive liquids. In 1978 the landfill's license was revoked and the site was subsequently placed on the National Priorities List under the Comprehensive Environmental Response, Compensation and Liability Act of 1980 (CERCLA). A remedial investigation (2) was conducted in 1983 and concluded that:

- the soils around the site;
- the groundwater under the site;
- the sediments in Lebanon Creek adjacent to the site;

had been contaminated by the landfill.

Samples were obtained from several seeps surrounding the landfill and the results showed that the leachate contained up to 2000 mg/L of dissolved organics. The leachate was pumped from a deep depression into a tank truck and transported from New Lyme to Cincinnati for experimentation using the RBC.

PROJECT DESCRIPTION (FIGURE 1)

A pilot sized RBC that contains 1000 m^2 (11,000 square feet) of surface area which is roughly 10% the scale of a full sized unit (100,000 square feet) is located at EPA's T&E Facility (3). The diameter is 3.6 m (12 ft), identical to a full scale unit, but the length is only 1 m (3.3 ft) whereas a full scale unit is 7.6 m (25 ft).

The RBC was operated in a batch mode. The leachate was transferred from a storage tank to a mix tank where the volume was measured. The nutrients were then added for specific experiments. The contents were pumped into the RBC, and the RBC was operated at a constant speed of 1.5 rpm. When the reaction was complete, the contents were returned to the mix tank and then fed to the clarifier for solids removal. The overflow went to the receiving tank, where the treated leachate was stored until the analytical results showed that the material was within the allowable discharge limits.

Effluent limitations on the treated leachate were imposed by the City of Cincinnati's Mill Creek Treatment Facility (MCTF) as well as by laboratory prescribed contaminant levels. Both sets of limitations had to be met before the treated leachate was disposed of in the MCTF sewers. The effluent limitations set by the MCTF were:

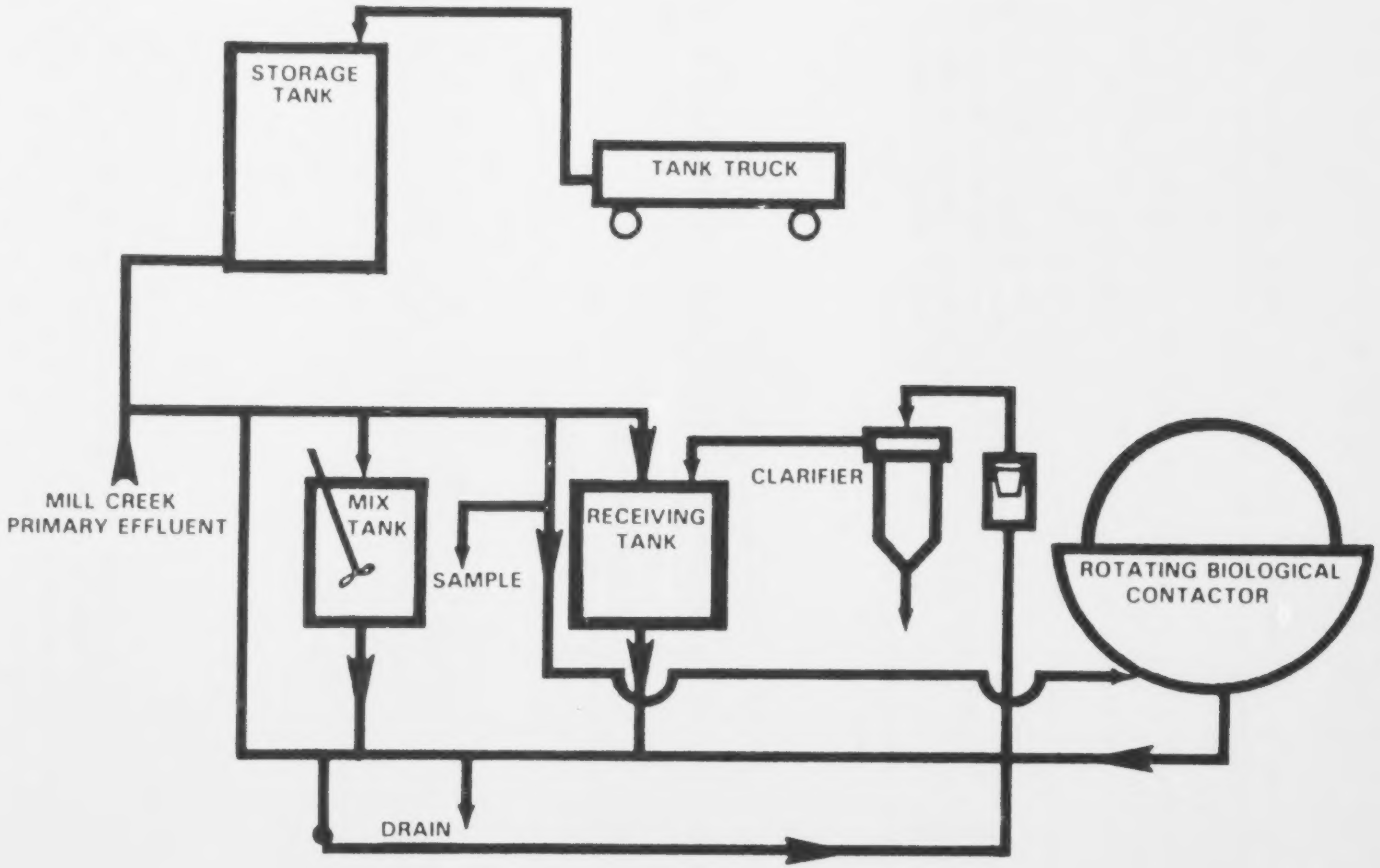

STORAGE TANK
TANK TRUCK
MILL CREEK PRIMARY EFFLUENT
MIX TANK
SAMPLE
RECEIVING TANK
CLARIFIER
ROTATING BIOLOGICAL CONTACTOR
DRAIN

Figure 1 **RBC Flow Schematic**

- total organic halides (TOX) $\leq$ 5 mg/L;
- vapor space organics (VSO) $\leq$ 300 ppm (4);
- 6 < pH < 10.

The internally applied limits were based on achieving a soluble gross organics level that would be equivalent to or less than a relatively high strength raw wastewater:

- soluble biochemical oxygen demand (SBOD) $\leq$ 100 mg/L;
- dissolved organic carbon (DOC) < 100 mg/L;
- soluble chemical oxygen demand (SCOD) $\leq$ 300 mg/L.

The underflow from the clarifier was analyzed for priority pollutants and drummed for disposal at a permitted landfill. We did experience a potentially unsafe incident with the drummed sludge. A drum bulged during storage. A gas analysis showed a high concentration of methane, which was probably caused by anaerobic degradation of the sludge. The pH of the sludge was then raised to 12 by adding caustic to deactivate the biomass and this action prevented a recurrence.

RESULTS

EXPERIMENTAL CONDITIONS

There were 8 experiments conducted with New Lyme leachate that varied in:

- volume of leachate fed to the RBC;
- ratio of leachate to primary effluent (L/PE);
- nutrient addition to the leachate;
- biomass condition (thickness, appearance, acclimation).

The initial runs used a combination of leachate and primary effluent to allow for acclimation of the biomass which was formed with primary effluent from the MCTP (5). The initial runs also used 2800 L (750 gal) instead of 3800 L (1000 gal) in order to conserve leachate. Nutrients were added to the leachate for experimentation to study this effect on the reaction. A fixed ratio of carbon (C)/nitrogen (N)/phosphorus (P) of 100/5/2 was used in three of the runs. These experimental variations are summarized in Table 1.

REACTION RATE

The reaction rate was determined by following the drop in the DOC with time (6). A plot of experiments 1 and 4, are shown in figure 2, and experiments 3 and 5 are displayed in figure 3. Experiments 2 and 7 are shown in figure 4. Experiment 6 is not included in the figures because its purpose was to determine the mass of volatile organics that was stripped by the RBC without any biomass. Experiment 8 is omitted because the leachate had undergone spontaneous biodegradation in the storage tank and was not

Figure 2. Disappearance of DOC With Time
Experiments 1 and 4

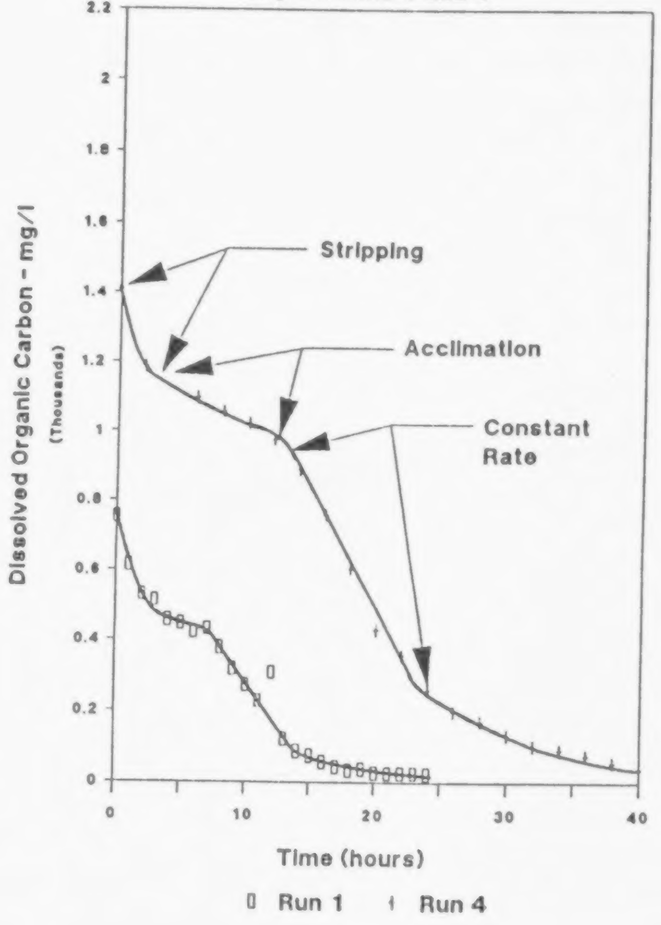


Figure 3. Disappearance of DOC With Time
Experiment 3 and 5

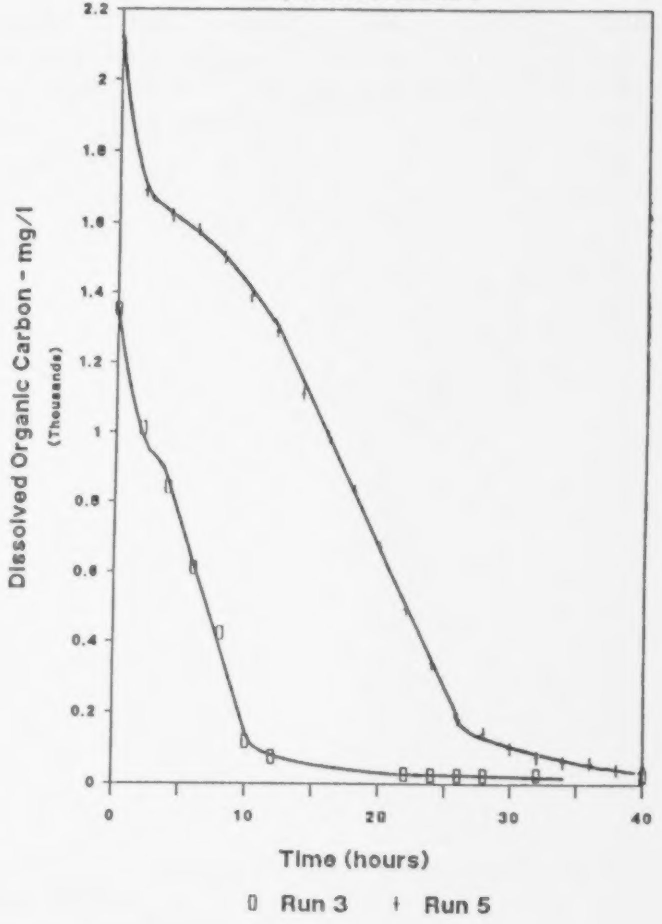


Figure 4. Disappearance of DOC With Time
Experiment 2 and 7

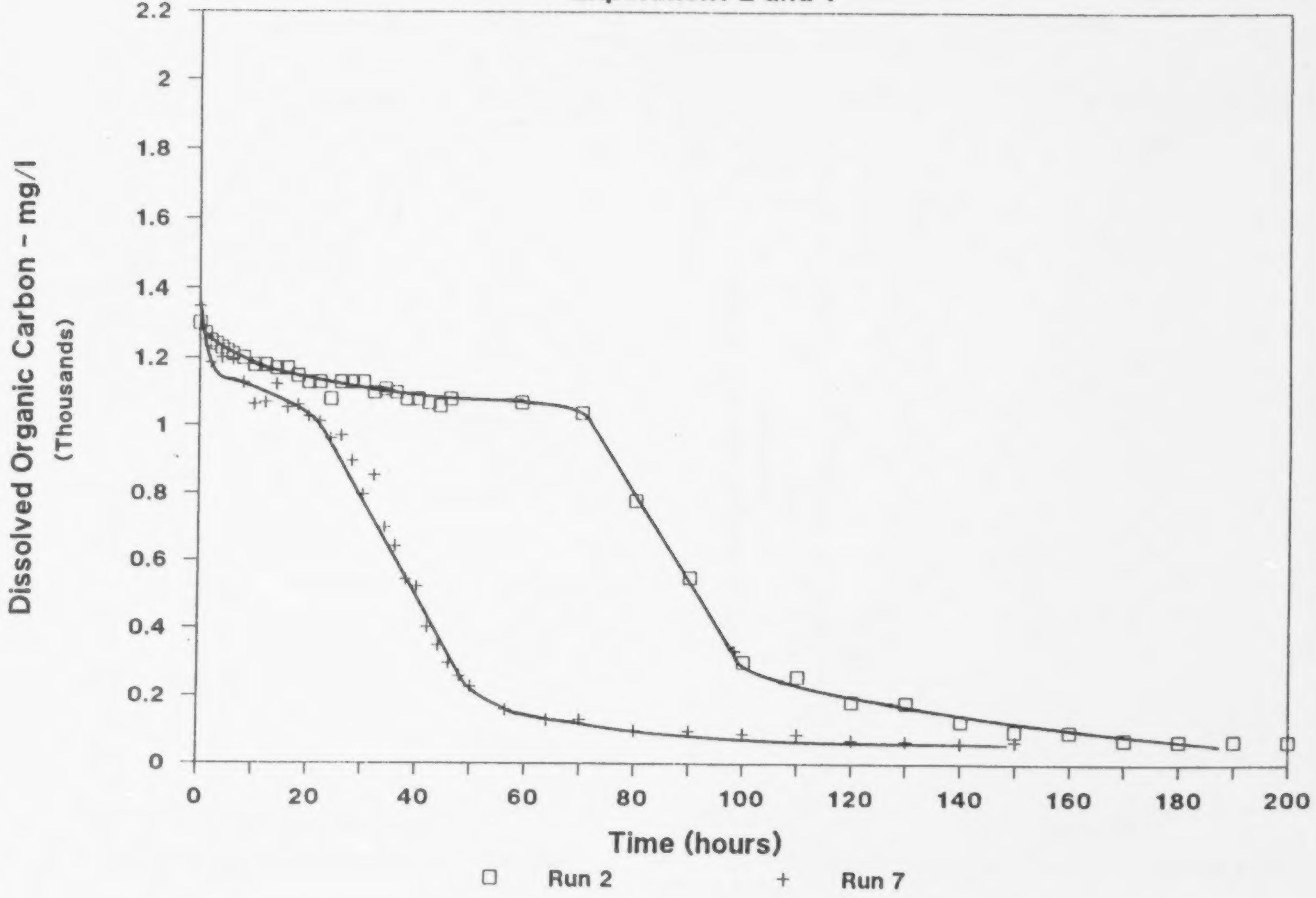


TABLE 1. EXPERIMENTAL CONDITIONS

Runs	Total Vol. Gal.	Ratio Leachate/PE Gal/Gal	Nutrient Addition	Ratio C/N/P	Biomass	Comments
01	750	250/500	No	---	No Acclimation	
02	750	500/250	No	---	Poor	
03	750	500/250	Yes	100/5/2	Satisfactory	
04	750	500/250	No	---	Satisfactory	
05	1,000	1,000/0	Yes	100/5/2	Satisfactory	
06	1,000	1,000/0	No	---	None	Volatile organics stripping run
07	1,000	1,000/0	Yes-N/No-P	100/5/0	No Acclimation	
08	1,100	1,100/0	Yes	100/5/2	No Acclimation	

representative of New Lyme leachate. The DOC at the start of experiment 8 had dropped to 280 mg/L, whereas the DOC for experiment 6 was 1780 mg/L.

The figures show an initial drop in the DOC concentration and this is attributed to the volatile organics being stripped from solution (see Figure 2, Experiment 4). There is evidence of this drop-off in each of the experiments. To verify this assumption, experiment 6 was operated without biomass and both the exhaust air from the RBC and the leachate in the RBC were analyzed. Both analyses confirmed that volatile organics were being stripped from the leachate. Provisions may be necessary to capture the volatile organics from an RBC to prevent air contamination when treating leachates with an RBC.

After stripping there was a period with a reduced reaction rate which was attributed to acclimation of the biomass to the leachate (see Figure 2, Experiment 4). There was only a slight drop in DOC during this time interval. The acclimation period varied but was especially evident in experiments 2 and 7 where the acclimation period lasted for 20 and 40 hours, respectively. The lengthy acclimation period for experiment 2 was attributed to an inadequate biomass. Prior to the start of experiment 2 the biomass was observed to be reddish-brown and spotty with a noticeable decrease in thickness, indicating that considerable sloughing-off of the biomass had occurred. The extended acclimation period for experiment 7 was attributed to the fact that it followed the volatile organics stripping run where the biomass had been removed from the discs. Therefore there was no prior acclimation of the biomass to the leachate.

Following the acclimation period, the reaction progressed at a constant rate, as shown in Figure 2, Experiment 4 by the disappearance of DOC. The reaction rate varied for each experiment ranging from a high of 350 g DOC converted per hour to a low of 82 grams per hour. The two experimental runs that had rates equal or greater than 300 grams per hour contained adequate levels of both nitrogen and phosphorus and had an adequate acclimation period from previous runs. It appears that the nutrient addition for experiments 3 and 5 may have contributed to the high organic removal rate. However, additional cause and effect experiments are needed to verify that nutrients may influence the reaction rate. The reaction rates for the 6 experiments and the ratios of C/N/P are shown in Table 2.

TABLE 2. RATES OF REACTION AND NUTRIENT RATIOS

Expt.	DOC Removed g/h	Ratios
1	140	100/5.5/<.2
2	82	100/1/<.2
3	350	100/5.5/1.4
4	180	100/1.1/<.2
5	300	100/5/2
7	120	100/6.7/<.2

Note: The C/N/P ratios shown in Table 2 are different from the earlier values given when describing the experimental conditions. The values in this Table reflect the contribution of the primary effluent and the leachate.

POLLUTANT REMOVALS

The experiments with New Lyme leachate were analyzed for typical biological parameters and priority pollutants. The removal of gross organics was determined by analyzing the influent and effluent for DOC, SBOD, SCOD, TOC, total BOD (BOD$_T$) and COD$_T$. Other biological parameters that were analyzed included suspended solids (SS) and volatile suspended solids (VSS), as well as the nutrient chemicals, both the nitrogen series and phosphorus (7).

The priority pollutant levels for untreated New Lyme leachate were compared with the effluents from the RBC after each experiment and on occasion compared with the sludge from the clarifier. Several volatile organics that were present in measurable quantities were identified during the priority pollutant analyses and their removals were occasionally followed during the RBC experiments. These results indicated that the removals of the pollutant by the RBC was effective for all the contaminants. The gross organics, as represented by DOC, SBOD and SCOD, were reduced to levels approaching a treated municipal secondary effluent.

A summary chart is shown in Table 3 for the biological parameters. The data for experiments 2, 3 and 4 were averaged since they were all run at the same leachate/PE ratio.

Only in the effluent from experiment 1 was a priority pollutant, methylene chloride, detected. Otherwise the biological treatment was effective for converting the priority pollutants into innocuous products.

Sludge samples were analyzed following experiments 2 and 5. Toluene was the only priority pollutant identified both times as present in the sludge. It was not determined whether the toluene was present in the liquid or solid phase. However, since toluene was not detected in the effluent, it is assumed that the toluene was associated with the solids in the sludge.

CONCLUSIONS

The study on treating the New Lyme leachate with an RBC showed very good removals/conversions of the organics and several experiments had reaction rates that were very satisfactory. The RBC is an effective process for leachate treatment.

- The RBC is an effective treatment process for reducing the organics in New Lyme leachate.
- Priority pollutants were converted and/or stripped from the leachate during treatment.
- The effluent quality is equivalent to a secondary treated effluent from a municipal wastewater treatment plant.
- Nutrient addition, at ratios of C/N/P of 100/5/2, shows evidence of favorably influencing the reaction rate.
- Volatile organics are stripped from the leachate by the RBC action when operated in a batch mode.
- The RBC experiences a period of inactivity near start-up that is assumed to be caused by the need for the biomass to acclimate to the leachate.

The RBC offers a high degree of treatment for processing leachates from a hazardous waste site. Additional research is needed such as

TABLE 3. REMOVAL OF POLLUTANTS FROM NEW LYME LEACHATE

	Experiment No. 1				Experiments No. 2, 3, 4				Experiment No.			
	L/PE = 1L/2L				L/PE = 2L/1L				5		7	
	L* mg/L	PE mg/L	INF mg/L	Cl EFF mg/L	L mg/L	PE mg/L	INF mg/L	Cl EFF mg/L	L mg/L	EFF mg/L	L mg/L	CL EFF mg/L
SBOD	3400.	120	1200	<2.0	4800.	140.	3000.	4.4	2700.	4.0	2000.	3.2
BOD_T			1600	---	5000.	230.	3300.	8.4	3000.	6.6	2600.	21.
DOC	2100.	100	760	17.	2200.	82.	1400.	19.	2000.	17.	1400.	45.
TOC			830	19.	2200.	102.	1500.	20.	2100.	19.	1400.	52.
SCOD	5900.	290	2100	66.	5200.	220.	3700.	50.	5200.	33.	3800.	190.
COD_T			2200	69.	5600.	370.	4100.	78.	---	---	4000.	220.

---

*L = Leachate
PE = Primary Effluent
INF = Influent to RBC
Cl EFF = Clarifier Effluent

determining the degree of organic stripping while the biodegradation reaction is occurring, and the validation of rapid reaction rate kinetics when the nutrients are controlled at their theoretical levels.

REFERENCES

1. Draft Report of "Treatability Testing and Field Investigation Report New-Lyme Landfill," U.S. Army Corps of Engineers, Omaha District, January, 1987.
2. Final Remedial Investigation New Lyme Landfill Site, Ashtabula County, Ohio, CH_2M-Hill, February 6, 1985.
3. Brenner, R. C., Heidman, J. A., Opatken, E. J., Petrasek, A. C., "Design Information on Rotating Biological Contactors," EPA-600/2-84-106, June 1984.
4. "Vapor Space Organics," In-House method developed by the Metropolitan Sewer District of Greater Cincinnati, Industrial Waste Section, Cincinnati, Ohio.
5. Opatken, E. J., Howard, H. K., Bond, J. J., "Biological Treatment of Hazardous Aqueous Wastes," Second International Conference on New Frontiers for Hazardous Waste Management, September 1987.
6. Opatken, E. J., "An Alternative RBC Design - Second Order Kinetics," Environmental Progress, Vol. 5, No. 1, February 1986.
7. Antonie, R. L., Fixed Biological Surfaces - Wastewater Treatment, CRC Press, 1976.

TRIAL BURN REPORTING AND DEVELOPMENT OF PERMIT CONDITIONS

by: Sonya M. Stelmack
U.S. EPA, Office of Solid Waste
Washington, DC 20460

C. C. Lee
U.S. EPA, Office of Research & Development
Cincinnati, OH 45268

ABSTRACT

A technical guidance manual has been developed to assist permit writers in one of the most complex and time-consuming portions of the incinerator permitting process: evaluation of trial burn results and translation of these results into facility-specific operating conditions. The manual is also intended to assist applicants in designing a trial burn operational protocol and in reporting of trial burn data.

The manual sets forth the key operating parameters which are important to maintaining compliance with the incinerator performance standards. The parameters are divided into groups depending on whether they are based on trial burn results or manufacturer's specifications, and whether they should activate automatic waste feed cutoff when exceeded. Methods for setting levels for these permit conditions and for planning trial burns are described.

The guidance also describes the information which should be included in a trial burn report and provides suggested standard reporting forms. These forms are expected to increase uniformity of trial burn reports and reduce the need for the permit writer to request additional information, thereby speeding the review process.

DISCLAIMER

The guidance document described in this paper is a draft, and has not been formally released by the U.S. Environmental Protection Agency. Neither the guidance document nor this paper should be construed to represent Agency policy. The guidance is being circulated for comments on its technical merit and policy implications.

INTRODUCTION

Subtitle C of the Resource Conservation and Recovery Act (RCRA) requires the U. S. EPA to develop, promulgate, and implement regulations which control the generation, transportation, and treatment, storage, and disposal (TSD) of hazardous waste. Regulations promulgated under RCRA, at 40 CFR Part 264, Subpart O, specify the following performance standards which facilities treating hazardous waste by incineration are required to meet:

1) 99.99% destruction and removal efficiency (DRE) for each principal organic hazardous constituent (POHC) in its permit for each waste feed (or 99.9999% for dioxin listed wastes)

2) 99% removal efficiency of HCl or 1.8 kg/hr of HCl emissions, whichever is greater

3) particulate emissions less than 180 mg/dscm, corrected to 7% oxygen

The regulations also require that fugitive emissions be controlled by keeping the combustion zone totally sealed, maintaining negative draft, or an equivalent alternative means of control.

Facilities seeking a permit to incinerate hazardous waste are required to demonstrate the unit's capability to meet the performance standards during a trial burn. Since a permitted incinerator's compliance with these performance standards cannot be monitored over the long term, the conditions at which the incinerator operated during the trial burn are included in the incinerator's permit as conditions for continuing operation. Compliance with these operating conditions is then deemed to be compliance with the performance standards. An incinerator must be operated with a system to automatically cut off waste feed to the incinerator when operating conditions deviate from limits established in the permit.

Although the regulations specify four operating parameters which must be set as permit conditions based on the trial burn (carbon monoxide level, waste feed rate, combustion temperature, and an indicator of combustion gas velocity), it is left to the permit writer to determine how to translate the trial burn data into permit conditions, and to determine which additional parameters should be set as permit conditions in order to assure continued compliance. Because of the technical complexity of setting permit conditions for hazardous waste incinerators, and the flexibility the regulations allow in setting these conditions, there has been a lack of consistency in the operational portions of incinerator permits issued across the country. Further, an excessive number of permit conditions may severely limit the incinerator's flexibility of operation, while too few permit conditions may not provide adequate assurance that the performance standards will continue to be met.

APPROACH

The major goals in developing the guidance were to develop a nationally consistent, sound technical approach to the setting of operational conditions in incinerator permits which would maintain proper performance while allowing a reasonabledegree of operational flexibility. Technical rationales were to be stated in the document so that it would also serve as a training tool, and to enable the permit writer to identify and address cases where specific portions of the guidance may not apply. Various operating parameters thought to have an effect on achievement of the incinerator performance standards were considered for inclusion in the guidance. These conditions were evaluated based on technical knowledge, and, where necessary, consensus of engineering judgment, to develop a set of operating parameters to be set in incinerator permits which would meet with the above goals. "Back-up" parameters which would unnecessarily limit the permittee's flexibility to operate the incinerator were avoided.

Management of the project was a cooperative effort by the Office of Solid Waste and the Hazardous Waste Engineering Research Laboratory (HWERL) of the Office of Research & Development. The document was prepared by three contractors: Acurex, general coordination and engineering aspects, MRI, sampling and analysis aspects, and EER, engineering analysis. Because of the desire to issue guidance which was both technically sound, and practical from an implementation standpoint, a significant amount of outside input was incorporated.

DESCRIPTION

This paper reflects the content of the final draft guidance. Minor changes may be made to the guidance prior to publication, based on a final review. The guidance document presents the key control parameters, shown in Table 1, which should be monitored during the trial burn and for which limits should be set in the incinerator permit. The parameters are divided into three groups.

Group A parameters are continuously monitored parameters interlocked to automatic waste feed cutoff. Most of these

TABLE 1 CONTROL PARAMETERS

Group A

Continuously monitored parameters are interlocked with the automatic waste feed cutoff. Interruption of waste feed is automatic when specified limits are exceeded. The parameters are applicable to all facilities.

1. Minumum temperature measured at each combustion chamber exit
2. Maximum CO emissions measured at the stack or other appropriate location
3. Maximum flue gas flowrate or velocity measured at the stack
4. Design pressure maintained in primary combustion chamber
5. The following as applicable to the facility
   - Minimum differential pressure across particulate venturi scrubber
   - Minimum water/liquor flowrate and pH to absorber and dry scrubber
   - Minimum KVA settings to ESP (wet/dry) and KV for ionized wet scrubbers (IWS)
   - Minimum and maximum pressure differential across baghouse

Group B

Parameters do not require continuous monitoring and are thus not interlocked with waste feed cutoff systems. Operating records are nevertheless required to ensure that trial burn worst-case conditions are not exceeded.

6. Maximum total halides and ash feedrate to the incinerator system
7. POHC incinerability limits
8. Maximum size of containerized to primary chamber
9. Minimum particulate scrubber blowdown rate

Group C

Limits on these parameters are set independently of trial burn test conditions. Instead, limits are based on equipment manufacturers' design and operating specifications and are thus considered good operating practices. Selected parameters do not require continuous monitoring and are not interlocked with the waste feed cutoff.

10. Maximum total heat input capacity for each chamber
11. Liquid injection chamber burner settings:
    - Maximum viscosity of pump
    - Maximum burner turndown
    - Minimum atomization fluid pressure
12. Maximum APCE inlet gas temperature

parameters are based on trial burn conditions. A minimal amount of lag time may be incorporated into the limits for these parameters by use of averaging times or delay times, following guidelines in the document. This allows for normal fluctuations in process parameters, and may allow time for corrective action to be taken either by the automatic process control system or manually. Group B parameters are set to ensure that the "worst case" conditions demonstrated in the trial burn are not exceeded during continuing operation. These parameters are not linked with automatic waste feed cutoff and are not continuously monitored, but instead must be recorded in the facility operating record. Group C parameters are set independently of trial burn results, based on equipment manufacturers' design and operating specifications. These parameters are not continuously monitored or linked to automatic waste feed cutoff.

Group A Parameters

Temperature is a key parameter of incinerator performance due to its influence on reaction kinetics, and is a required incinerator permit condition under RCRA regulations. The minimum temperature limit is generally set from the lowest temperature trial burn test at which compliance was demonstrated. Combustion chamber temperatures are required by the regulations to be tied to automatic waste feed cutoff. For a two-chamber incinerator, minimum temperatures would be set for each chamber. When minimum temperatures are not maintained in the primary and secondary chambers, or in the secondary chamber only, waste feed must be cutoff to both chambers. However, if only the primary chamber falls below its minimum temperature, waste may still be fed to the secondary chamber.

Carbon monoxide concentration in the stack gas is also a parameter which the regulations specifically require. CO is used as an indicator of the degree of mixing achieved in the incinerator, and is related, by definition, to combustion efficiency. Separate guidance on setting permit limits on CO in order to minimize emissions of PIC's (products of incomplete combustion) is being prepared by EPA.

The hazardous waste incinerator regulations require that the permit specify limits for an indicator of combustion gas velocity. Combustion gas velocity is directly related to the gas residence time in the incinerator, which is known to be one of the key parameters of combustion. Residence time becomes more critical at lower combustion temperatures. For this reason, the limit on maximum combustion gas velocity should be based on the maximum trial burn value measured during the lowest temperature test.

A waste feed rate limitation is required by RCRA regulations primarily to minimize the potential loss of efficiency from overloading the combustion chambers. For low heating value wastes, the limits are taken from the trial burn test with the minimum temperature, since an increase in the waste feed rate may cause a decrease in temperature. Maximum waste feed rate for high or medium heating value wastes will be set independently of temperature.

The requirement in the regulations to control fugitive emissions is addressed by a permit requirement that the unit design pressure is maintained. Incinerator chambers designedto operate under negative draft (induced draft) would be required by the permit to maintain negative draft. Forced draft or positive pressure incinerators must be well sealed and a maximum pressure would be set in the permit based on the unit design pressure.

The guidance recommends that control parameters for air pollution control equipment (APCE) be set to maintain the particulate and acid scrubbing capability demonstrated during the trial burn. For each type of APCE component, one key parameter was chosen to be tied to automatic waste feed cutoff. For example, since the principal operating parameter controlling ESP collection efficiency is the power utilization, or KVA, the minimum KVA demonstrated during the trial burn at the highest ash feed rate will be set as the permit limit.

Group B Parameters

One of the key principles behind conducting a trial burn is that the incinerator should operate under the most severe conditions it is expected to encounter for the duration of its permitted operation. Group B parameters are included in the guidance to assure that the incinerator will not operate at more taxing conditions than those at which it demonstrated compliance during the trial burn.

Parameters affecting APCE performance included in Group B are total ash and chlorine loading to the incinerator. These parameters affect the concentrations of particulate and HCl at the APCE inlet and the physical and chemical properties of the gas. The ash and chlorine loadings are limited to the maximum rate demonstrated in the trial burn. A minimum scrubber blowdown rate will also be set based on the trial burn, since suspended and dissolved solids in recycle water can be re-entrained into the flue gas, contributing to particulate emissions.

The Subpart O regulations require that POHCs (Principal Organic Hazardous Constituents) be designated for each waste feed. The required DRE must then be demonstrated for the POHCs during the trial burn. Since the POHCs must be representative of the waste feed, they are chosen based on factors such as difficulty to incinerate and concentration in the waste feed. The operator is then limited in the permit to burning only waste containing hazardous constituents no more difficult to incinerate than the POHCs for which compliance was demonstrated during the trial burn. The heat of combustion of the hazardous constituents has been used to rank the incinerability of compounds on the premise that compounds with a lower heat of combustion are more difficult to burn. Field data indicate, however, that other ranking systems may exhibit a better correlation with incinerability. The guidance presents a draft ranking of the incinerability of Appendix VIII compounds prepared by the University of Dayton Research Institute based on thermal stability at low oxygen (TSLoO2) conditions. Additional laboratory and field testing of the TSLoO2 ranking are currently being conducted under a cooperative agreement between EPA and UDRI.

A limit on the maximum size of containerized waste fed to the incinerator is also recommended in order to prevent oxygen depletion from the sudden release of volatiles. The containerized waste fed during the trial burn should be representative, with respect to volatile content, of the waste the facility will be burning under the permit.

Group C Parameters

Group C parameters were formulated based on the need to ensure that incinerator operation adheres to good combustion and APCE operating practices. To allow a reasonable degree of flexibility and to avoid over-complication of the trial burn, limits for these parameters are to be based on manufacturer's design and operating specifications rather than the trial burn settings.

To maintain proper automation of liquid waste and promote efficient mixing, burner operational settings for liquid injection and afterburner chambers will be limited to manufacturer's specifications. These conditions include maximum waste viscosity, minimum automation fluid pressure, and maximum burner turndown. A minimum waste heating value will be set in the permit for liquid injection chambers where 100% of the heat input comes from the waste feed. Total heat input to the incinerator will be limited to the incinerator design heat input capacity.

The guidance recommends limiting APCE inlet gas temperature due to its effect on the APCE performance as well as to prevent equipment deterioration. For example, the minimum inlet temperature to a baghouse would be based on the dew point of the incoming gases, while a maximum temperature would be set based on manufacturer specifications for the type of fabric used.

Other Permit Conditions

The guidance also includes additional conditions related to waste feed cutoff. The permit should require that minimum temperature be maintained in the secondary combustion chamber after a waste feed cutoff until wastes remaining in the unit are burned out. This would necessitate use of auxiliary fuel, but must not conflict with the unit's flame safety management system. The guidance recommends a condition requiring quarterly reporting of automatic waste feed cutoffs, reasons for the cutoffs, and corrective actions taken.

Translating Trial Burn Results into Permit Conditions

The guidance presents a strategy for determining the limits on operating parameters and converting them into permit conditions. The goal in translating the trial burn results into permit conditions is to assure the incinerator is operating in a manner sufficiently similar to the successful trial burn conditions to maintain compliance, but still allow adequate operational flexibility. The approach commonly employed is patterned around "mode-based" operation. The permit contains a different set of operating conditions for each waste combination the facility will burn. This approach is best suited for a facility dedicated to treating a well-defined set of uniform composition hazardous wastes.

The above approach, however, is not practical for facilities such as commercial facilities, which burn a wide variety of wastes. The guidance presents an approach to developing a universal set of operating conditions which defines the allowable range of operation for burning all of the wastes in the facility permit. The difficulty in using the trial burn data to develop a universal set of operating conditions is that it is usually not possible to maintain worst-case conditions for all permit parameters at a single operating point. Thus, permit conditions must be developed from data obtained at several operating points.

In the general approach set forth in the guidance, the parameters are divided into three groups:

1. Control parameters set from trial burn data that are related to waste destruction
2. Control parameters set from trial burn data that are related to APCE performance
3. Control parameters that are independent of trial burn data

Limits on parameters are set according to the above hierarchy. The groupings of these parameters are shown in Table 2. Permit limits must only be set from trial burn tests that show compliance with the performance standards. Limits should be set using these basic rules of thumb regarding "worst case" conditions. The maximum combustion gas velocity should be set from the trial burn test conducted at the minimum temperature. The maximum feed rate of each low heating value waste stream to each combustion chamber should be that demonstrated during the minimum temperature test. The maximum feed rate of high heating value wastes and the maximum combined feed rate should be the maximums demonstrated at any point.

TABLE 2

Control Parameter Classifications

Waste Destruction-Related Parameters Set From Trial Burn Data
- minimum temperature
- maximum waste feed rate
- maximum combustion gas velocity
- maximum size of containerized waste

APCE Performance-Related Parameters Set From Trial Burn Data
- minimum differential pressure across venturi scrubber
- minimum water/liquor flow rate and pH to absorber
- minimum KVA for ESP and KV for ionized scrubber- minimum and maximum baghouse pressure differential
- maximum chlorine and ash feed rate
- minimum particulate scrubber blowdown rate

Trial Burn-Independent Parameters
- maximum CO concentration
- maximum primary combustion chamber pressure
- maximum total heat input
- liquid injection chamber burner settings
- maximum APCE inlet gas temperature

Permit limits for APCE parameters relating to particulate collection should be set from the trial burn test at the maximum inorganic ash feed rate and the maximum flue gas flow rate, since ash feed rate determines the load to the ACPE, and increasing the flue gas flow rate may increase entrainment of particulate matter. Minimum liquor flow rate to the absorber and minimum pH to the absorber should be set from the trial burn test at the maximum total halides feed rate and the maximum flue gas flow rate.

In some instances, it may not be possible to set the conditions in the manner described above due to interrelationships among parameters which prevent certain conditions from being achieved at the same time. The guidance presents an approach to estimate, through calculations, whether the effect of setting the conditions based on less than worst-case runs will be significant. For example, if the permit limit for the maximum flue gas velocity is to be set from a data point other than the minimum temperature test, then the permit writer would do calculations to determine whether it is likely that the flue gas flow rate at the minimum temperature could be increased to the maximum flue gas flow rate without causing DRE to decrease below 99.99%. This is done by relating flue gas flow rate to residence time to DRE assuming a first-order reaction.

The guidance emphasizes the importance of planning the trial burn to obtain the desired permit conditions. The applicant and permit writer should agree, prior to the trial burn, on what permit conditions will result from the trial burn as planned, assuming compliance is demonstrated. This will allow the applicant to go back and make modifications to the trial burn plan, if necessary, to obtain the desired operating conditions.

Trial Burn Reporting

The permit writer is often faced with reviewing a trial burn report which is incomplete or which is not structured in a way that is conducive to finding the information necessary to evaluate compliance and set permit conditions. The permit writer may need to go back to the applicant to request clarification or additional data, which slows down the review process. To assist both applicants and permit writers, the guidance describes the information which should be included in the trial burn report, and presents a trial burn report format. Example reporting forms for the design, process, and performance data required in a trial burn report have been developed, and are presented in the document.

SUMMARY

The Guidance on Trial Burn Reporting and setting Permit Conditions has been developed to assist permit writers in translating trial burn results into site-specific operational conditions in an incinerator permit. These parameters are presented in the document, along with guidance on how to develop permit operating conditions using the trial burn data.

The guidance will also assist applicants in planning their trial burns to address the key operating parameters that must be measured and the necessity to test "worst-case" operations. This will enable applicants to tailor their propose operating conditions to the needs of their facility. One of the key points made by the guidance is that the permit writer and applicant should agree, prior to the trial burn, on what permit conditions will result from the trial burn as planned. In this way, it can be determined whether it is necessary to make modifications to the plan in order to obtain the desired operating conditions.

ACKNOWLEDGMENTS

This guidance document was prepared for the U.S. Environmental Protection Agency's Office of Solid Waste (OSW) and the Office of Research and Development (ORD) under the overall direction of Ms. Sonya Stelmack of OSW Permits and State Programs Division, with technical review by Dr. C.C. Lee and Donald Oberacker of ORD Hazardous Waste Engineering Research Laboratory. Ms. Robin Anderson also contributed to the project.

The principal investigator was Mr. Carlo Castaldini, assisted by Dr. Leo Weitzman and Mr. Andy Murphy, all of Acurex. Technical contributors were Dr. Randall Seeker and Mr. Wyman Clark of EERC, and Mr. Andrew Trenholm and Mr. Gary Hinshaw of MRI.

Additional technical contributions and review were provided by a panel of incineration experts from selected EPA Regional Offices. This panel included Mr. Gary Gross of Region III, Ms. Betty Willis of Region IV, Mr. Y.J. Kim of Region V, and Mr. John Hart of Region IX.

EPA wishes to acknowledge and thank the American Society of Mechanical Engineers for providing review comments on drafts of the guidance document.

REFERENCES

A.D. Little, Inc. Sampling and Analysis Methods for Hazardous Waste Combustion. First Edition. Prepared for EPA under EPA Contract No. 68-02-3211 (124). PB84-155845, December 1983.

Mitre Corporation. Guidance Manual for Hazardous Waste Incinerator Permits. EPA-SW-966, PB84-10000577, July 1983.

Monsanto Research Corporation. Engineering Handbook for Hazardous Waste Incineration. EPA-SW-889, PB81-248163, September 1981.

Clark, W.D., W. R. Seeker, and C.C. Lee. Engineering Analysis of Hazardous Waste Incineration, Energy and Mass Balance. In

Proceedings of the Twelfth Annual Research Symposium on Land Disposal, Remedial Action, Incineration and Treatment of Hazardous Waste. EPA/600/9-86/022, 1986. pp. 360-368.

Dellinger, B., et.al. Examination of Fundamental Incinerability Indices for Hazardous Waste Destruction. Proceedings on Incineration and Treatment of Hazardous Waste. EPA-600/9-85/028, September 1985.

Hesketh, H.E., Air Pollution Control. Ann Arbor, Michigan, Ann Harbor Science Publishers, 1980.

Brunner, Calvin R. Incineration Systems. Van Nostrand Reinhold Company, New York, 1984.

ROTARY KILN INCINERATION:

THE EFFECT OF OXYGEN ENRICHMENT ON FORMATION OF TRANSIENT PUFFS DURING BATCH INTRODUCTION OF HAZARDOUS WASTES

William P. Linak, Joseph A. McSorley
Combustion Research Branch, MD-65
Air and Energy Engineering Research Laboratory
U.S. Environmental Protection Agency
Research Triangle Park, NC 27711

Jost O.L. Wendt
Department of Chemical Engineering
University of Arizona
Tucson, AZ 85721

James E. Dunn
Department of Mathematical Sciences
University of Arkansas
Fayetteville, AR 72701

ABSTRACT

Experiments on a 73 kW (250,000 Btu/hr) rotary kiln incinerator simulator equipped with a prototype oxygen enrichment burner were performed to determine the effect of oxygen enrichment on the magnitude and intensity of transient puffs emitted during batch introduction of contained liquid surrogate waste (toluene) on corncob sorbent. Results show that the effect of oxygen enrichment at constant temperature is to decrease the transient puff size but that increases in kiln temperature associated with oxygen enrichment can offset this and cause net increases in the transient emissions. This effect is likely due to increases in the rate of waste volatilization. These results were especially true for particulate matter and are consistent with previous results without oxygen enrichment.

INTRODUCTION

Oxygen enrichment has long been applied to many industrial combustion processes in order to increase product yields and thermal efficiency. The use of oxygen in hazardous waste incineration to augment or enrich oxidant levels in the combustion zones has the potential to improve the destruction and removal efficiencies (DREs) of the principal organic hazardous constituents (POHCs), minimize the formation of products of incomplete combustion (PICs), and allow for better control of the combustion process.

The use of oxygen enrichment in rotary kiln incinerators is of interest as a potential method of minimizing transient failure conditions caused by the batch introduction of waste material. Rotary kiln incinerators are unique in that they are designed to allow a portion of their waste load to be charged in batch rather than continuous mode. In this batch mode of operation, solid wastes and "containerized" liquid wastes are introduced through entrance chutes, typically cocurrent with the gas flow. Kiln angle and rotation speed continuously expose fresh surface for oxidation, determine the residence times of non-combustible materials, and provide for continuous ash removal. Upon entry into the incinerator, the liquid waste container, typically cardboard, plastic, or steel drums, ruptures or burns, exposing the contents to the hot kiln environment. The liquid then rapidly vaporizes and reacts with the excess oxygen present in the combustion gases from the continuous primary flame. A possible kiln failure condition arises when the evolution of waste gases from the ruptured container is more rapid than the rate at which the stoichiometric amount of oxygen can be supplied from the primary flame. This transient overcharging condition, unique to batch mode systems, can lead to a "puff" of incompletely destroyed organic material which must subsequently be destroyed by the system afterburner. Under circumstances when the afterburner cannot destroy the quantity of organic material produced, this puff leads to a system failure.

This paper discusses results of part of an in-house program at the U.S. Environmental Protection Agency (EPA) directed toward gaining engineering insight into potential problem areas related to rotary kiln incineration. General objectives are to delineate fundamental combustion phenomena that are important in the generation of transient puffs from batch fed wastes. It is not within the scope of this work to do exhaustive POHC, PIC, or DRE analyses. The specific objectives of the work presented here are to determine the effects of oxygen enrichment through the primary flame on the formation of transient puffs, caused by the batch introduction of a contained surrogate liquid waste (toluene) on sorbent into a rotary kiln incinerator simulator. Further, the tests and analysis techniques attempt to separate the individual effects of dilution, temperature, oxygen flow, and oxygen partial pressure. Results from tests utilizing this simulator to examine transient puffs from prototype solid plastic wastes and contained surrogate liquid wastes without oxygen enrichment have been presented previously.[1,2]

This paper is divided into four sections. Following the Introduction, the Experimental Approach is discussed. Next, Results and Discussion of the experimental study are presented. Finally, the findings from this study are summarized in the Conclusions.

EXPERIMENTAL APPROACH

The EPA rotary kiln incinerator simulator has been described in detail previously,[1,2] and therefore, is not presented again here. It has been established that the simulator, although sized at only 73 kW (250,000 Btu/hr), exhibits the salient features of full-scale units with thermal ratings 20 to 40 times larger. The simulator matches the volumetric heat release, gas-phase residence time, and temperature profile of many full-scale units, and yet is flexible enough to allow parametric testing. A schematic drawing of the simulator is presented in Figure 1.

The water-cooled prototype burner is designed to produce stable flames utilizing oxidant streams ranging from 22 to 100 percent oxygen. The burner provides for separate introduction of natural gas, air, and oxygen with turndown ratios of at least 1 to 10. The burner is easily ignited and capable of rapid response to changes in the fuel, air, or oxygen flows. Liquid oxygen was provided in cryogenic Dewar tanks, with each tank containing approximately 127 m^3 (4500 scf) of gaseous oxygen.

Contained batch charges to the rotary kiln are introduced through a sliding gate/ram assembly located downstream of the continuous natural-gas-fired oxygen-enriched main burner as shown in Figure 1. Quantification of the transient puff produced requires the real-time measurement of system response variables. These dependent variables include peak responses of O_2, CO, CO_2, NO_x, and total volatile hydrocarbon concentrations (THC) measured by continuous flame ionization detection (FID) and reported in equivalent parts per million methane. Other dependent variables include the time-integrated responses of the THC analyzer and particulate filter weight. At constant sampling conditions, these variables are proportional to the total mass emitted in the transient puff. Weighed desiccated quartz filters and the heated particulate filter system upstream of the THC analyzer were used to collect particulate samples. Volatile hydrocarbons are defined as those in the gas-phase at 420 K (300 °F), the temperature of the heated sample line.

Charges to the kiln were kept constant for all tests presented in this paper. Only the natural gas, air, and oxygen flows to the prototype burner were varied by test design to cause changes in the oxygen flow, partial pressure, and stoichiometric ratio. Charges to the kiln consisted of 100 g (0.22 lb) of toluene on 135 g (0.30 lb) of ground corncob sorbent sealed in a 45 g (0.10 lb) cylindrical uncoated 1 qt (0.95 l) cardboard container. Similar charges were used in previous work by this group.[2] Toluene was chosen because it yields large chlorine-free puffs to which the FID is very sensitive. Toluene also produces large particulate loadings. A charge mass of 100 g (0.22 lb) was chosen because it provides large puffs which did not greatly exceed the FID linear response region of zero to 10,000 ppm (reported as methane) for the conditions tested.

As with the previous studies, a portion of the experimental design was based on response surface experimentation.[3] This methodology allows, on the basis of one experiment involving a minimal number of trials, determination of an empirical relationship between the response and the controlled variables in the experimental region. For the first set of experiments, the flows of

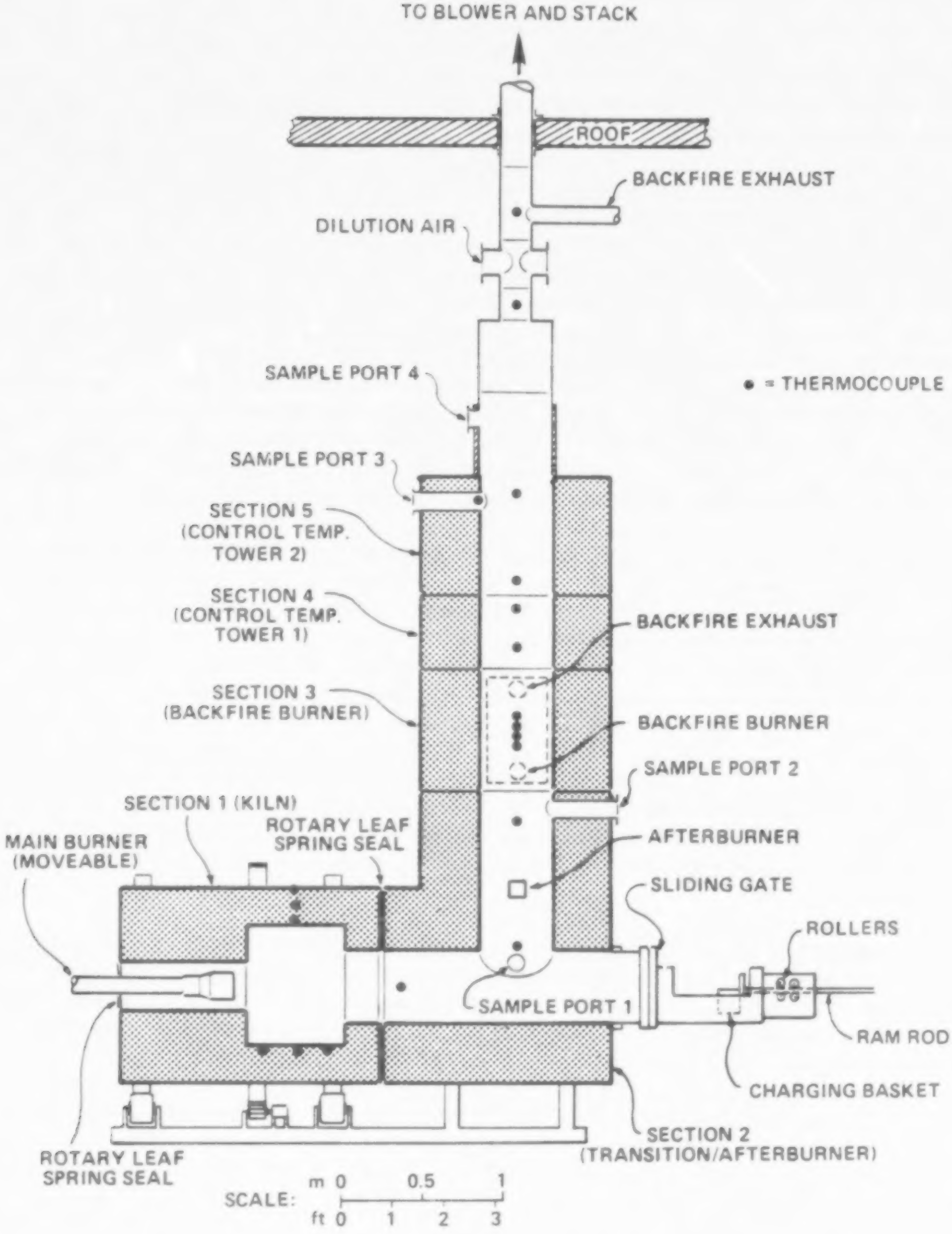

TO BLOWER AND STACK
ROOF
BACKFIRE EXHAUST
DILUTION AIR
SAMPLE PORT 4
● = THERMOCOUPLE
SAMPLE PORT 3
SECTION 5 (CONTROL TEMP. TOWER 2)
SECTION 4 (CONTROL TEMP. TOWER 1)
BACKFIRE EXHAUST
SECTION 3 (BACKFIRE BURNER)
BACKFIRE BURNER
SAMPLE PORT 2
SECTION 1 (KILN)
ROTARY LEAF SPRING SEAL
MAIN BURNER (MOVEABLE)
AFTERBURNER
SLIDING GATE
ROLLERS
SAMPLE PORT 1
RAM ROD
CHARGING BASKET
SECTION 2 (TRANSITION/AFTERBURNER)
ROTARY LEAF SPRING SEAL
SCALE:
m 0 0.5 1
ft 0 1 2 3

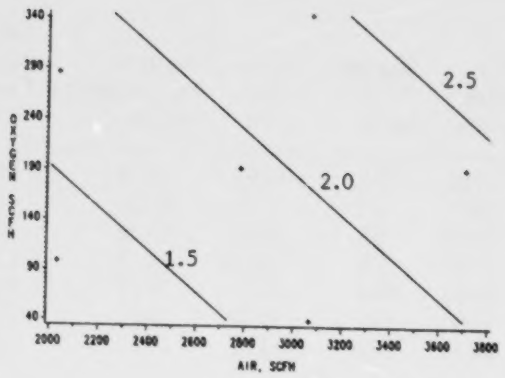
Figure 1. EPA incinerator simulator, cutaway view.

oxygen and air were chosen as the controlled or independent variables. The natural gas auxiliary fuel feed rate (kiln load) was held constant. These variables are of intrinsic interest to an incinerator operator because they are directly controlled. By defining these flow rates to the burner, several other system parameters are defined. These calculated variables include; stoichiometric ratio, primary flame oxygen enrichment, total flow (approximately inversely proportional to residence time), primary flame oxygen and nitrogen flows, adiabatic flame temperature, post primary flame oxygen flow, and post primary flame oxygen partial pressure. Throughout this first set of experiments, the natural gas flow was held constant at 5.66 m^3/hr (200 scfh), and the oxygen and air flows to the burner were varied by experimental design to examine six combinations (plus one duplicate) of oxygen and air flows. Figure 2 presents the combinations of air (57.5 to 105.0 m^3/hr, 2030 to 3707 scfh) and oxygen (1.13 to 9.74 m^3/hr, 40 to 344 scfh) flows that form the second order rotatable pentagonal design (data points denoted by +). Figure 2 also shows that these air and oxygen flows correspond to a range of calculated stoichiometric ratios from 1.3 to 2.4 (Figure 2a), post flame oxygen flows from 3.29 to 16.37 m^3/hr (116 to 578 scfh) (Figure 2b), and post primary flame oxygen partial pressures from 5.0 to 16.0 percent (Figure 2c). A summary of the final trial matrix including the controlled and derived system variables is presented in Table I.

The seven (six plus one duplicate) experiments, described in Figure 2 and Table I, were conducted in the following manner. The desired natural gas, air, and oxygen flows were set, and the kiln was allowed to thermally equilibrate to the new condition for at least 5 hours. Charges were prepared, sealed, and introduced to the kiln at approximately 10 minute intervals. Between 10 and 12 replicate charges were recorded and averaged for subsequent statistical analysis. Kiln rotation speed, kiln pressure, and burner position were kept constant at 0.5 rpm, -37.4 Pa (-0.15 in. H_2O), and -0.34 m (-13.5 in.) inside the kiln front wall, respectively. Note that the effect of the kiln alone is being examined. There was neither afterburning nor external heating of the combustion products. We are trying to determine the behavior of the kiln and, subsequently, the relative role of the afterburner to ensure adequate destruction.

Based on the results of the first set of response surface experiments, a second and third series of two dimensional tests were performed in an attempt to separate the individual effects of stoichiometric ratio, post flame oxygen flow, and post flame oxygen partial pressure. The design of the response surface experiments was limited. It is evident from Figure 2 that, for the response surface experiments, the three oxygen parameters (stoichiometric ratio, post flame oxygen flow, and post flame oxygen partial pressure) are highly correlated with each other and vary in the same manner. In fact, due to the constant auxiliary fuel load used for these experiments, specification of either stoichiometric ratio or post flame oxygen flow defines the other. To separate these effects, two sets of additional experiments were designed, varying the auxiliary fuel load. These trial matrices are presented in Tables II and III. The trial matrix in Table II, was designed to vary the post flame oxygen flow and partial pressure independently while holding stoichiometric ratio constant. The trial matrix in Table III, varies stoichiometric ratio and post flame oxygen partial pressure while holding

(a) STOICHIOMETRIC RATIO



(b) POST FLAME OXYGEN FLOW,SCFH

(c) POST FLAME OXYGEN PARTIAL PRESSURE,%

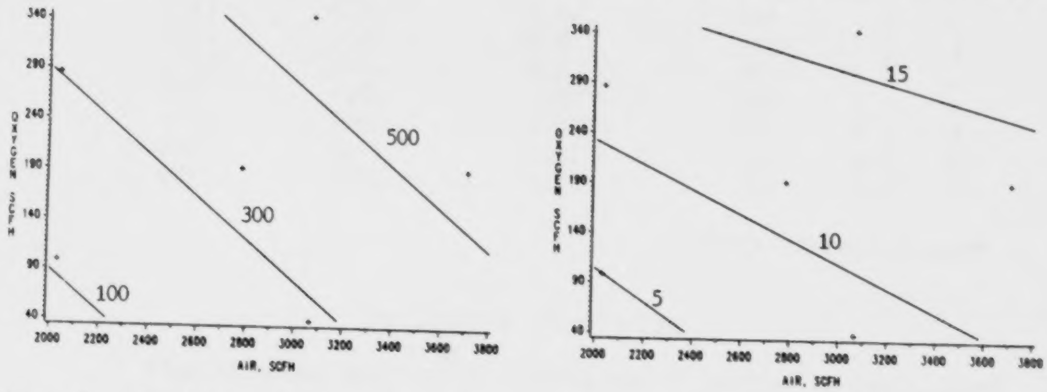


Figure 2. Contours of constant (a) stoichiometric ratio, (b) post flame oxygen flow, and (c) post flame oxygen partial pressure over the test region examined by data set 1 (response surface experiments). Trial matrix points denoted by +.

post flame oxygen flow constant. The individual data sets were collected in the same manner as described previously for the response surface experiments, and other kiln operating parameters were held constant as described above. It was hoped that the additional experiments might indicate whether post flame oxygen flow or post flame oxygen partial pressure had the greater influence on transient puffs. While the post flame oxygen flow (total molar oxygen flow to which the waste charge is exposed) may be varied without oxygen enrichment, variation of the post flame oxygen partial pressure is limited without oxygen enrichment.

TABLE I. TRIAL MATRIX FOR DATA SET 1
(RESPONSE SURFACE EXPERIMENTS, CONSTANT GAS FLOW).

Test	Gas flow, scfh	Air flow, scfh	Oxygen flow, scfh	Total flow, scfh	Oxygen enrichment, percent	Total oxygen flow, scfh	Nitrogen flow, scfh
1	200	3707	192	4099	24.8	967	2932
2	200	3066	40	3306	21.9	681	2425
3	200	2030	98	2328	24.5	522	1606
4	200	2030	286	2516	30.7	710	1606
5	200	3066	344	3610	28.9	985	2425
6	200	2780	192	3172	26.0	773	2199
7	200	2780	192	3172	26.0	773	2199

Test	SR*	Post flame oxygen flow, scfh (FO_2)	Post flame oxygen partial pressure, percent (PO_2)	Adiabatic flame temp, K	Measured kiln exit temp, K
1	2.4	560	13.7	1454	1125
2	1.7	274	8.3	1687	1172
3	1.3	116	5.0	2125	1201
4	1.7	304	12.1	2017	1200
5	2.4	578	16.0	1584	1151
6	1.9	367	11.6	1732	1181
7	1.9	367	11.6	1732	1159

*stoichiometric ratio

RESULTS AND DISCUSSION

Results are presented in two parts. First, the measured puff is considered without correction for any dilution effects. This represents what must be handled by the afterburner and is of interest to operators and designers of rotary kiln systems. Next, two sets of data are presented that have been corrected for dilution effects. These represent the rates of volatile release from the waste.

Set 1: Dilution Effects Not Considered

Full quadratic models with respect to air and oxygen flows were fitted to the data from the first set of experiments (Table I) using weighted least squares, where the weights were equal to the number of replicates. These models, obtained using the preprogrammed procedures in SAS (Statistical Analysis System), should not be considered unique since other models might attain fits essentially identical to those reported here. Once determined, these models can be described pictorially through response surface plots. The response surface plots are unique to the data they describe. Figure 3 presents these contour plots for the dependent variables: volatile hydrocarbon

TABLE II. TRIAL MATRIX FOR DATA SET 2
(TWO DIMENSIONAL EXPERIMENTS, CONSTANT STOICHIOMETRIC RATIO).

Test	Gas flow, scfh	Air flow, scfh	Oxygen flow, scfh	Total flow, scfh	Oxygen enrichment, percent	Total oxygen flow, scfh	Nitrogen flow, scfh
8	150	2732	40	2922	22.0	611	2161
9	150	1249	350	1749	38.2	611	988
10	200	3707	40	3947	21.7	815	2932
11	200	2224	350	2774	31.7	815	1759
12(20)	250	4679	40	4969	21.6	1018	3701
13(21)	250	3196	350	3796	28.7	1018	2528
14	300	5656	40	5996	21.5	1222	4474
15	300	4173	350	4823	27.0	1222	3301

Test	SR*	Post flame oxygen flow, scfh (FO_2)	Post flame oxygen partial pressure, percent (PO_2)	Adiabatic flame temp, K	Measured kiln exit temp, K
8	2.0	306	10.5	1508	1000
9	2.0	306	17.5	2107	1047
10	2.0	408	10.3	1494	1112
11	2.0	408	14.7	1891	1190
12(20)	2.0	510	10.3	1487	1213
13(21)	2.0	510	13.4	1782	1286
14	2.0	613	10.2	1482	1247
15	2.0	613	12.7	1716	1320

*stoichiometric ratio

peak area (peak area) (Figure 3a), volatile hydrocarbon peak concentration (peak height) (Figure 3b), carbonaceous particulate filter weight (filter weight) (Figure 3c), and CO peak concentration (peak CO) (Figure 3d) versus oxygen and air flows. Full quadratic models were able to explain total response variances (r^2) of 0.9485, 0.8992, 0.9993, and 0.9610 for peak area, peak height, filter weight, and peak CO, respectively. The variance is a measure of the dispersion of the response, defined as the square of the standard deviation. Evident from Figure 3 is that, for all the response variables, transient puffs are reduced at higher air and oxygen levels. Peak area and peak height responses at high air and oxygen flows (upper right corners) are approximately nine and five times less, respectively, than at low flows (lower left corners). Filter weight response decreases by a factor of four over the same region, and peak CO by a factor of six. It is important to note, however, that a portion (but not all) of these response reductions can be explained by simple dilution. Total flow changes by a factor of 1.8 over this experimental region, but due to the fact that we are trying to characterize the inlet conditions to which an afterburner system must be able to respond, we have not corrected these data for dilution.

TABLE III. TRIAL MATRIX FOR DATA SET 3
(TWO DIMENSIONAL EXPERIMENTS, CONSTANT POST FLAME OXYGEN FLOW).

Test	Gas flow, scfh	Air flow, scfh	Oxygen flow, scfh	Total flow, scfh	Oxygen enrichment, percent	Total oxygen flow, scfh	Nitrogen flow, scfh
16	150	3708	40	3898	21.7	815	2933
17	150	2225	350	2725	31.7	815	1760
18	200	4194	40	4434	21.6	917	3317
19	200	2711	350	3261	29.9	917	2155
20(12)	250	4679	40	4969	21.6	1018	3701
21(13)	250	3196	350	3796	28.7	1018	2528
22	300	5165	40	5505	21.5	1119	4086
23	300	3682	350	4332	27.8	1119	2912

Test	SR*	Post flame oxygen flow, scfh (FO_2)	Post flame oxygen partial pressure, percent (PO_2)	Adiabatic flame temp, K	Measured kiln exit temp, K
16	2.7	510	13.1	1239	931
17	2.7	510	18.7	1575	1011
18	2.2	510	11.5	1380	1071
19	2.2	510	15.6	1693	1151
20(12)	2.0	510	10.3	1487	1213
21(13)	2.0	510	13.4	1782	1286
22	1.8	510	9.3	1571	1255
23	1.8	510	11.8	1844	1340

*stoichiometric ratio

The response curves in Figure 3 can be compared with the contours of constant stoichiometric ratio, post flame oxygen flow, and post flame oxygen partial pressure, presented in Figure 2. It is not surprising that puff intensities should be reduced at higher oxidant levels and higher total flows. In addition to the effect of dilution, providing higher oxygen flows and higher oxygen partial pressures to the vaporizing waste cause fuel rich regions to be more difficult to achieve. However, without oxygen enrichment, it is often difficult in practice to operate at high stoichiometric ratios while maintaining kiln temperatures and flame stability due to the quenching effect of nitrogen. Also evident from Figure 3 is the fact that all three responses are more sensitive to changes in oxygen flow than to changes in air flow. Small changes in oxygen flow cause large changes in stoichiometric ratio, post flame oxygen flow, and post flame oxygen partial pressure, without significantly affecting the adiabatic flame temperature or gas-phase residence time. Conversely, large changes in air flow are necessary to effect changes in stoichiometric ratio or post flame oxygen flow. Without oxygen enrichment,

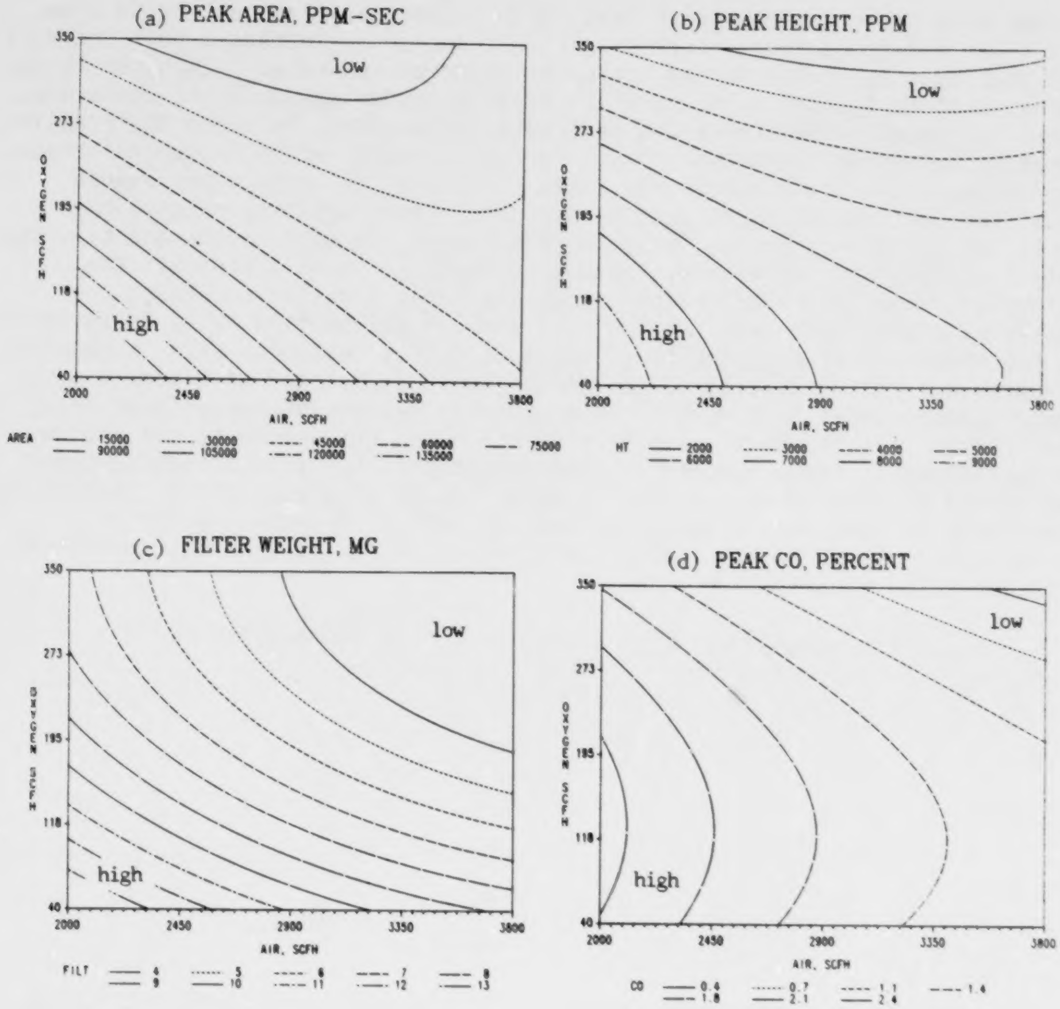


Figure 3. Data set 1 response surface contour plots for (a) volatile hydrocarbon peak area, (b) volatile hydrocarbon peak height, (c) particulate filter weight, and (d) peak CO. Data are not corrected for dilution.

oxygen partial pressure is limited by atmospheric conditions. Additionally increasing air flow also significantly decreases the adiabatic flame temperature, flame stability, and gas-phase residence time.

The response curves of Figure 3, however, do not describe the individual effects of the derived system variables. It is important to establish the individual effects of stoichiometric ratio, oxygen enrichment, residence time, adiabatic flame temperature, measured kiln temperature, post flame oxygen flow, and post flame oxygen partial pressure on the response variables.

It has been shown previously[1,2] that, with respect to transient puffs from batch waste introduction, increasing kiln temperature increases puff intensity and that this is likely due to increased vaporization rates. This result is in contrast to typical kiln operating practice under steady-state operation, where increased temperatures are desirable because they increase the kinetic rates of oxidation reactions. Thus, for batch waste, while oxygen enrichment may increase the flame stability, flame stoichiometry, post flame oxygen flow, and post flame oxygen partial pressure, increased temperatures may drive the waste into the gas-phase more rapidly. We must try to quantify the relative magnitudes of each of these mechanisms. Figure 4 presents the calculated adiabatic flame temperatures and total flow rates through the rotary kiln simulator over the range of air and oxygen flow rates investigated by the first set of experiments (Table I). System residence time is roughly proportional to the inverse of the total flow. Comparison of Figure 4 with the response curves in Figure 3 shows that the regions of lowest peak area, peak height, filter weight, and peak CO responses correspond to the regions of low adiabatic flame temperature and high total flow (low residence time). The effect of high total flow can be explained by simple dilution. Additionally, the effect of increased temperature with respect to transient puffs is counterintuitive to normal steady-state incineration practice but consistent with increased vaporization rates.

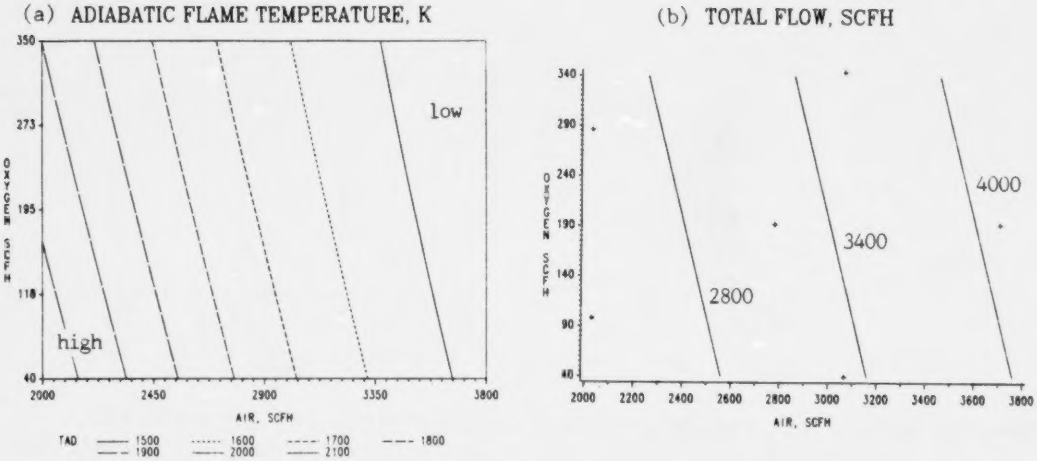


Figure 4. Contours of constant (a) adiabatic flame temperature and (b) total flow over the region examined by data set 1 (response surface experiments). Trial matrix points denoted by +.

To determine the relative importance of each of these controlled, measured, and derived variables on the response variables, single term linear models were constructed from the data of the first set of experiments (Table I). Table IV presents the response variance explained for each independent variable examined individually. The results show that the three derived variables of most significance in explaining the variance in the response variables are post flame oxygen flow, stoichiometric ratio, and post flame oxygen partial pressure. As previously mentioned, the experimental design was such that all

TABLE IV. FRACTION OF VARIANCE (r^2) OF DATA SET 1 EXPLAINED BY SINGLE TERM LINEAR MODELS.

Variable	Peak area ppm-sec CH_4	Peak height ppm CH_4	Filter weight mg	Peak CO ppm
Post flame oxygen flow, scfh (FO_2)	0.8494	0.8389	0.9460	0.8618
SR*	0.8510	0.8395	0.9467	0.8636
Post flame oxygen partial pressure, percent (PO_2)	0.9359	0.8632	0.9374	0.7887
Total oxygen flow, scfh	0.7633	0.8170	0.5519	0.5078
Residence time, 1/scfh	0.5199	0.6204	0.6903	0.7284
Adiabatic flame temperature, K	0.5148	0.6267	0.6938	0.7317
Total flow, scfh	0.4380	0.6089	0.6596	0.6920
Oxygen enrichment, percent	0.4759	0.5917	0.1894	0.2094
Measured kiln exit temperature, K	0.3293	0.4614	0.5935	0.5258
Air flow, scfh	0.2382	0.4513	0.5114	0.5423

*stoichiometric ratio

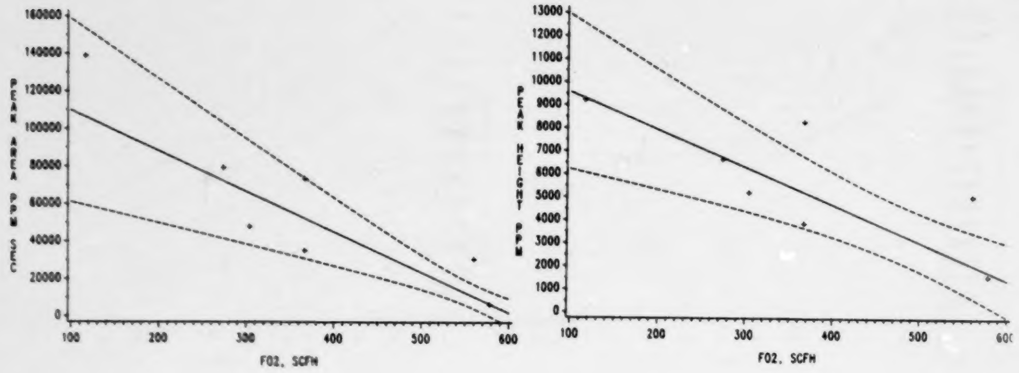
three of these variables are highly correlated and indicate the oxygen available to the vaporizing waste. Of lesser importance are the variables: total oxygen flow, residence time, adiabatic flame temperature, total flow, primary flame oxygen enrichment, measured kiln temperature, and total air flow. These results indicate that, for the experimental region examined here, transient puffs can be reduced by providing increased oxygen to the waste, and that even though increasing the oxygen flow may change the temperature and residence time, the effects of increased available oxygen dominate. It is important to note that these data indicate only a secondary effect due to temperature, even though previous results[1,2] indicated that temperature has a major effect on the intensity of transient puffs from batch incineration. Calculated adiabatic flame temperatures for this experimental set vary from 1450 to 2000 K (2150 to 3140 °F), yielding an experimental range of 550 K (990 °F). In actuality, however, the measured kiln exit temperature varies only from 1125 to 1200 K (1565 to 1700 °F); therefore, this actual experimental range of 75 K (135 °F) may be insufficient to establish any temperature effects.

Figures 5 and 6 present the single term linear models for post flame oxygen flow and post flame oxygen partial pressure, respectively, versus peak area (Figures 5a and 6a), peak height (Figures 5b and 6b), filter weight (Figures 5c and 6c), and peak CO (Figures 5d and 6d). Again, due to the experimental design of the first data set, similar plots for stoichiometric ratio are identical to those for post flame oxygen flow. Figures 5 and 6 include the averaged data for each of the seven experimental conditions (denoted by +), as well as the 95 percent confidence regions around each linear model. All the data indicate decreasing response with increasing post flame oxygen flow (and stoichiometric ratio) and post flame oxygen partial pressure. Attempts were made to add additional linear and quadratic terms to the models; however, these additions did not significantly increase the variance explained. Again, note that a portion of these responses can be explained by simple dilution.

A possible disadvantage to oxygen enrichment for use in hazardous waste incineration is the potential to produce high concentrations of nitrogen oxides (NO_x) due to the increased temperatures and increased available oxygen. Effects of the latter may greatly exacerbate this problem if high nitrogen containing wastes are incinerated, although even if the waste contains little or no nitrogen, thermal fixation of ambient nitrogen may produce unacceptable quantities of NO_x. Figure 7 presents contours of baseline nitric oxide (NO) concentration over the region examined by the first experimental set (Table I). The data are presented as measured (Figure 7a) and corrected to 7 percent oxygen (Figure 7b) in the exhaust gas. Concentrations as high as 1500 ppm (at 7 percent oxygen) were determined for high oxygen operating conditions using natural gas auxiliary fuel only.

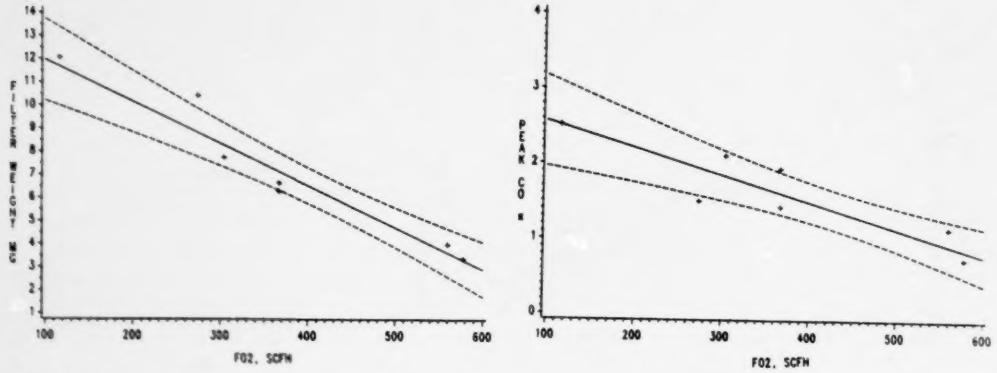
Sets 2 and 3: Corrected for Dilution Effects

As stated previously, the second and third data sets (Tables II and III) were intended to separate the individual effects of stoichiometric ratio, post flame oxygen flow, and post flame oxygen partial pressure. By varying the natural gas load to the kiln, experiments were designed in which these three parameters vary independently. The purpose was to determine the relative importance of the molar flow rate of oxygen to the waste charge (proportional to post flame oxygen flow) and the volumetric oxygen concentration available to the waste charge (equal to the post flame oxygen partial pressure). Two-dimensional plots of post flame oxygen flow and post flame oxygen partial pressure versus the response variables were prepared at constant stoichiometric ratio (SR=2.0). Additionally, similar plots of stoichiometric ratio and post flame oxygen partial pressure versus the response variables were prepared at



(a) PEAK AREA PPM-SEC: R^2 =0.849

(b) PEAK HEIGHT, PPM: R^2 =0.839

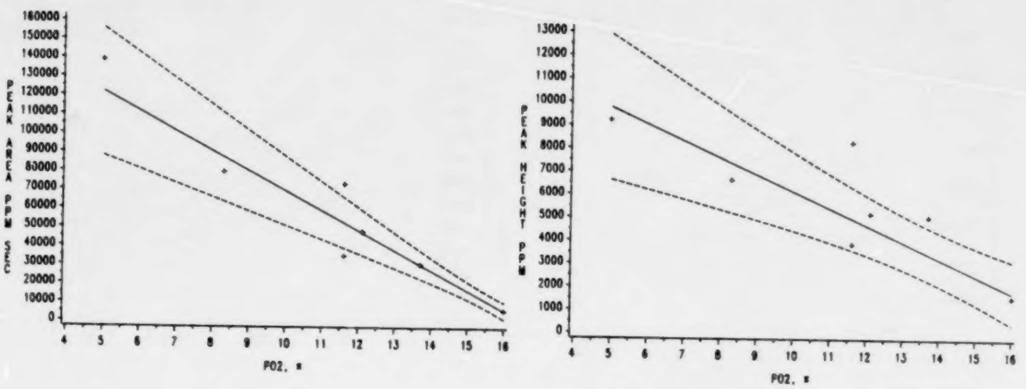


(c) FILTER WEIGHT, MG: R^2 =0.946

(d) PEAK CO, PERCENT: R^2 =0.862

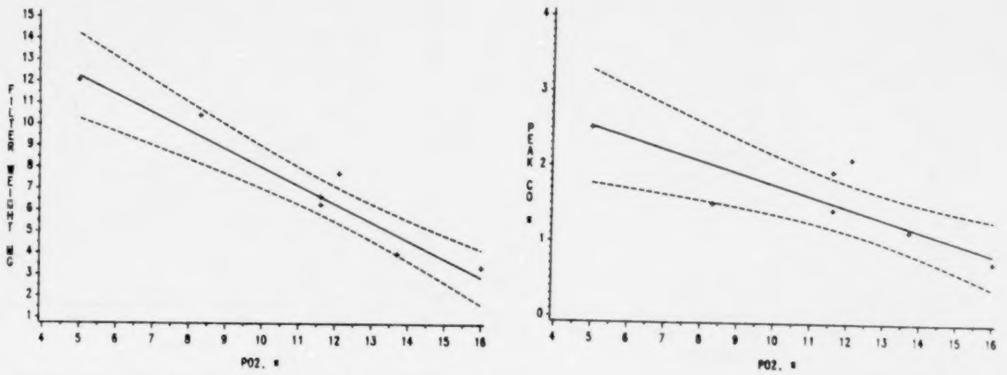
Figure 5. Single term linear models describing response of (a) volatile hydrocarbon peak area, (b) volatile hydrocarbon peak height, (c) particulate filter weight, and (d) peak CO versus post flame oxygen flow (FO_2). Averaged data from data set 1 (response surface experiments) denoted by +. Solid lines indicate best linear fit; dotted lines indicate 95 percent confidence region. Data are not corrected for dilution.

constant post flame oxygen flow (F02=14.4 m^3/hr, 510 scfh). These data were all corrected for dilution by normalization to a standard total flow of 113 m^3/hr (4000 scfh). These plots showed the data to be scattered, and no consistent trend existed between all of the response variables. A likely explanation for these inconsistent results is that, in addition to the effects of changes in the post flame oxygen flow and partial pressure, confounding influences due to large changes in kiln temperature are included. By changing the kiln load, necessary to effect changes in post flame oxygen flow and partial pressure, measured kiln exit temperatures vary over a wide range (320



(a) PEAK AREA PPM-SEC: R^2 =0.936

(b) PEAK HEIGHT, PPM: R^2 =0.863



(c) FILTER WEIGHT, MG: R^2 =0.937

(d) PEAK CO, PERCENT: R^2 =0.789

Figure 6. Single term linear models describing response of (a) volatile hydrocarbon peak area, (b) volatile hydrocarbon peak height, (c) particulate filter weight, and (d) peak CO versus post flame oxygen partial pressure (PO_2). Averaged data from data set 1 (response surface experiments) denoted by +. Solid lines indicate best linear fit; dotted lines indicate 95 percent confidence region. Data are not corrected for dilution.

K, 576 °F). It has been shown previously[1,2] that the effect of increased kiln temperature is increased transient emissions and that this is likely due to increased volatility. Data have also shown that for toluene, a known soot precursor, soot formation is disproportionately promoted over volatile hydrocarbon emissions with increasing temperature.[2] Due to the confounding influences of temperature, no conclusions can be drawn that separate the individual effects of post flame oxygen flow and partial pressure. However, overall, the effect of oxygen enrichment via the primary combustion chamber to minimize the emissions from transient puffs does not seem to be dramatic

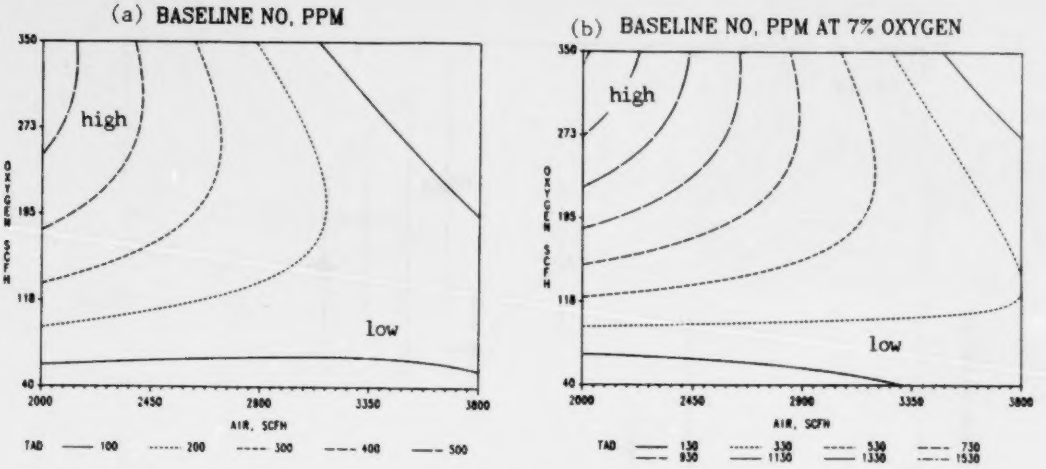


Figure 7. Contours of constant baseline NO flue gas concentration (a) as measured and (b) corrected to seven percent oxygen over the region examined by data set 1 (response surface experiments).

over the experimental region examined here. Indeed, it can be detrimental when the effects of temperature are included.

To illustrate that the effect of increasing kiln temperature can be detrimental to transient emissions, Figure 8 presents filter weight data from each of the second and third experiment sets (Tables II and III) versus measured kiln exit temperature. Data from experiments taken at constant stoichiometric ratio (SR=2.0) (Figure 8a) and constant post flame oxygen flow (FO_2=14.4 m^3/hr, 510 scfh) (Figure 8b) are presented. These data, relating to low oxygen flow/enrichment (open symbols) and high oxygen flow/enrichment (solid symbols), have been corrected for dilution by normalization to a standard total flow of 113 m^3/hr (4000 scfh). Data taken at similar kiln loads are connected. The data show fair correlation between filter weight and measured kiln exit temperature, and indicate a trend of increasing particulate emissions with increasing temperature over the experimental range examined here. The data may indicate some slight reduction in particulate emissions due to oxygen enrichment at similar kiln loads, as shown by the dotted lines on Figure 8. However, if the oxygen enrichment causes a dramatic increase in the kiln temperature, particulate emissions are actually increased. This is also illustrated in Figure 8 by comparison of all open or solid symbols.

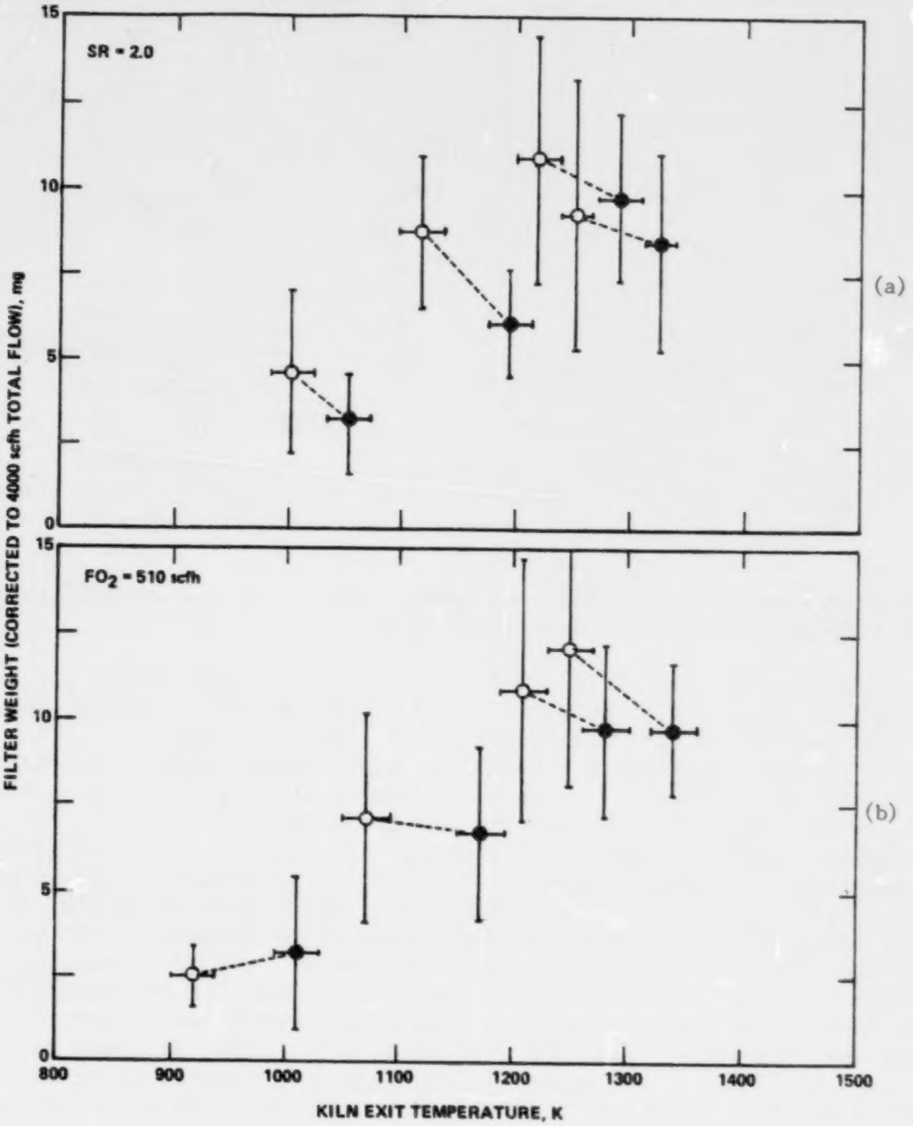


Figure 8. Results from data sets 2 and 3 (two dimensional experiments) showing the relationship between filter weight and measured kiln exit temperature for (a) constant stoichiometric ratio (SR) and (b) constant post flame oxygen flow (FO_2). Data are corrected to 4000 scfh total flow. Open symbols indicate tests at low oxygen flow/enrichment (1.13 m^3/hr, 40 scfh). Solid symbols indicate tests at high oxygen flow/enrichment (9.91 m^3/hr, 350 scfh). Tests at similar kiln load (natural gas flow) are connected.

CONCLUSIONS

The results of experiments involving the use of oxygen enrichment via the primary flame (primary combustion chamber) of a rotary kiln incinerator simulator feeding batch charges of contained liquid surrogate waste (toluene) on corncob sorbent are consistent with results previously presented by the authors.[1,2] A summary of the results from this study includes:

1. The phenomena associated with transient puff formation from the batch introduction of contained waste are fundamentally different from those associated with steady-state incineration. The realization of these differences is important in order to minimize organic emissions.

2. Although increased temperatures associated with oxygen enrichment may provide potential benefits for steady-state incineration, these increased temperatures are detrimental in controlling transient puffs from contained wastes. This was especially true for particulate emissions.

3. It is difficult to draw conclusions regarding the individual effects of stoichiometric ratio, or post flame oxygen flow, or post flame oxygen partial pressure due to the confounding effects of temperature.

4. When the effects of temperature are removed, oxygen enrichment causes a reduction, beyond simple dilution, in the magnitude and intensity of transient puffs from contained wastes.

5. If temperature increases can be controlled (e.g. by using advanced forms of process control), oxygen enrichment may cause net decreases in transient puff emissions. Results of planned tests on such a system at EPA's Combustion Research Facility in Arkansas may provide these answers.

6. Oxygen enrichment may cause unacceptable emissions of nitrogen oxides (NO_x) even at baseline conditions burning clean auxiliary fuel due to thermal fixation of ambient nitrogen. These emissions may be exacerbated if high nitrogen containing wastes are incinerated.

7. The data indicate that the rotary kiln serves primarily to pyrolize the waste into the gas-phase, and that complete oxidation is not likely in the primary chamber even with the help of oxygen enrichment. It may be desirable to operate the kiln at reduced temperatures in order to retard the rate of volatile release of waste species from the solid or liquid phase, and rely on the afterburner for complete organic destruction.

8. Efficient design and operation of afterburner systems for these incinerators are crucial in order to minimize organic emissions, especially with regard to transient emissions.

9. Oxygen enriched burners may be more useful when utilized as part of an afterburner system where increases in temperature are desired and do not cause increases in the rate of solid or contained liquid waste volatilization.

ACKNOWLEDGMENTS

The authors would like to thank EPA/AEERL's R.W. Lowans for his technical advice and assistance in the data collection phases of this project. Special thanks to R.E. Hall, Branch Chief, Combustion Research Branch, AEERL, for his guidance and support. The authors would also like to acknowledge the contribution of American Combustion, Inc., of Norcross, GA, who designed, fabricated, and installed a prototype version of their Pyretron burner on EPA's rotary kiln incinerator simulator. Additionally, the authors would like to acknowledge the contribution of Liquid Air Corporation of Countryside, IL, who provided the liquid oxygen for the tests. Finally, the authors would like to thank the EPA's Hazardous Waste Engineering Research Laboratory (HWERL) in Cincinnati, OH, for partial support of this work.

DISCLAIMER

The research described in this article has been reviewed by the Air and Energy Engineering Research Laboratory, U.S. Environmental Protection Agency, and approved for publication. The contents of this article should not be construed to represent Agency policy nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

REFERENCES

1. W.P. Linak, J.D. Kilgroe, J.A. McSorley, J.O.L. Wendt, J.E. Dunn, "On the Occurrence of Transient Puffs in a Rotary Kiln Incinerator Simulator: I. Prototype Solid Plastic Wastes," J. Air Pollut. Control Assoc. 37(1):54 (1987).

2. W.P. Linak, J.A. McSorley, J.O.L. Wendt, J.E. Dunn, "On the Occurrence of Transient Puffs in a Rotary Kiln Incinerator Simulator: II. Contained Liquid Wastes on Sorbent," J. Air Pollut. Control Assoc. 37(8):934 (1987).

3. C.R. Hicks, "Fundamental Concepts in the Design of Experiments," 2nd edition, Holt, Rinehart, and Winston Inc., New York, NY (1973).

PATHWAYS OF PIC FORMATION IN HAZARDOUS WASTE INCINERATORS

B. Dellinger, P. H. Taylor, D. A. Tirey, and J. C. Pan
Environmental Sciences Group
University of Dayton Research Institute
Dayton, Ohio 45469
and
C. C. Lee
Hazardous Waste Engineering Research Laboratory
US-EPA
26 W. Martin Luther King Drive
Cincinnati, Ohio 45268

ABSTRACT

There has been considerable controversy concerning the potential for emissions of toxic products of incomplete combustion (PICs) from incinerators burning hazardous organic materials. It appears that the relative emission levels of both undestroyed components of the waste feed and PICs are controlled by chemical reaction kinetics. Thus, a study of the various chemical reaction mechanisms that can lead to PIC formation is valuable in predicting and controlling PIC emissions from incinerators. At least three general mechanistic pathways may be defined that can result in the formation of thermally stable PICs: 1) concerted molecular elimination, 2) molecular attack by reactive radicals, and 3) radical-atom and radical-radical recombination involving thermodynamically stable species. Each class of reaction can result in the formation of PICs which have different "apparent" stability behavior. Examples of each type of reaction are presented, and some general conclusions concerning PIC emissions are discussed.

INTRODUCTION

Control of emissions of toxic organic compounds from incinerators burning hazardous materials is one of the major technical and sociological issues surrounding the further implementation of incineration as a waste disposal alternative.[1] Laboratory-, pilot-, and full-scale studies have produced data indicating that properly designed and operated facilities can achieve the destruction of toxic organic waste feed components to environmentally acceptable levels.[2-5] However, total organic emissions from the incinerator effluent are seldom fully characterized. This has led to both scientific and public concern over the possible emissions of toxic products of incomplete combustion (PICs) resulting from incineration of toxic materials under less than ideal conditions.[6,7] Thus, the ability to predict and test for possible PIC emissions is clearly desirable.

We have presented data that strongly suggest that the relative destructive efficiencies (DEs) of the principal organic hazardous constituents (POHCs) in the waste feed, i.e., their relative incinerability, are controlled by high-temperature thermal decomposition kinetics in the post-flame regions of the incinerator.[8,9] Along with other researchers, we have suggested that "pyrolysis pockets" in the post-flame zone are responsible for emissions of undestroyed POHCs.[8-10] This has led us to develop an index of POHC incinerability based on thermal stability measurements under oxygen-starved conditions which has successfully correlated with full-scale emissions data in numerous cases.[10,11] Unfortunately, this index does not address PIC emissions or the potential impact on apparent POHC DE when a POHC is also formed as a PIC during the combustion process. Available data strongly suggests compounds selected as POHCs can also be formed as PICs from other components of the waste or fuel feed. This can significantly impact POHC relative emission rates and explain many of the anomalies in laboratory predicted versus full-scale determined POHC incinerability.[9]

As a first step towards developing guidelines for predicting full-scale PIC emissions, we are producing PIC data on simple chlorinated hydrocarbons.[12] However, completion of a data base on PIC formation from Appendix VIII compounds is far in the future.[13] Consequently, we have begun to analyze theoretical routes for PIC formation in an effort to determine which routes are dominant and lead to common, thermally stable PICs that can be used for incinerator trial burn testing. The following paragraphs present a theoretical discussion of these routes along with exemplary experimental data and reaction kinetic calculations.

EXPERIMENTAL TECHNIQUE

The data presented in this manuscript were generated primarily with the Thermal Decomposition Analytical System (TDAS). Only a brief description of its design and operation is presented here, as a more detailed description is available in other reports and publications.[14,15] The thermal decomposition unit of the TDAS consists of a high-temperature fused silica tubular reactor in which a flowing gas stream, exhibiting a segregated flow pattern, can be exposed to temperatures as high as 1200°C for mean residence times of 0.5 to 6.0 sec. Reactor design ensures that samples experience a square-wave thermal pulse with a narrow residence time distribution. Heated fused silica transfer lines connect the insertion chamber to the reactor and the reactor to the effluent analysis system. The analytical function of the TDAS is conducted by a Hewlett Packard 5890B programmed temperature gas chromatograph (GC) and 5970A Mass Selective Detector (MSD). Data reduction is achieved with a HP 59970 ChemStation and the accompanying system software which includes an on-line NIH-EPA mass spectral library.

DISCUSSION OF PIC FORMATION MECHANISMS

From a purely chemical reaction kinetic viewpoint, one may classify known mechanisms of PIC formation into three general groups: 1) concerted molecular eliminations, 2) radical-molecule reactions, and 3) radical-atom or radical-radical recombination reactions. As illustrated in Table 1, these mechanisms occur in different regions of the incinerator and can result in PICs of different structure and stability. Consequently, the nature of PICs formed and their potential destruction will be dependent on the different exposure conditions. The reaction rates for PIC formation processes increase from zero- to second-order in the radical concentration as one proceeds from mechanism 1 to mechanism 3. Thus, stoichiometry and elemental composition of the waste/fuel feed may significantly impact PIC yields for radical-molecule and radical-radical reaction pathways.

TABLE 1

DESCRIPTION OF HAZARDOUS WASTE INCINERATOR PIC FORMATION ZONES AND DOMINANT PIC FORMATION MECHANISMS

ZONE	REACTION CONDITIONS	PIC MECHANISMS[a]
Preflame Zone	T = 200-1000°C R.T. < 1 sec $[O_2]$ = 0-50% EA[e]	Mechanism 1[b] Mechanism 2[c] Mechanism 3[d]
Flame Zone	T = 1000-1800°C R.T. < 1 sec $[O_2]$ = 50% EA[e]	Mechanism 2 Mechanism 1 Mechanism 3
Postflame Zone (afterburner)	T = 600-1100°C R.T. = 1-3 sec $[O_2]$ = 50-100% EA[e]	Mechanism 2 Mechanism 1 Mechanism 3
Cool Zone (APCD and stack)	T = 80-600°C R.T. = 2-20 sec $[O_2]$ = 3-9%	Mechanism 3

---

[a] PIC formation mechanisms listed in decreasing order of importance.

[b] Concerted molecular elimination reactions.

[c] Radical-molecule reactions.

[d] Radical-atom or radical-radical recombination reactions.

[e] Average values; localized deviations due to poor mixing can result in pyrolytic conditions.

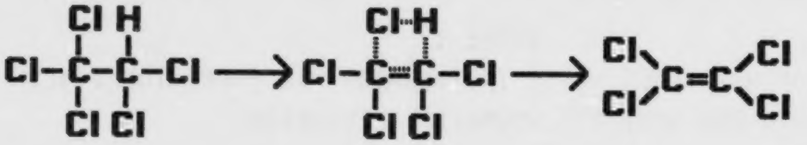
MECHANISM 1: CONCERTED MOLECULAR ELIMINATION REACTIONS

Concerted molecular elimination to form stable PICs is a subclass of unimolecular reactions, viz., reactions only involving the parent compound.[16] Since a second molecule or radical is not involved in the reaction, the PIC yield is dependent only upon time, temperature, and the Arrhenius parameters of the molecular elimination reaction:

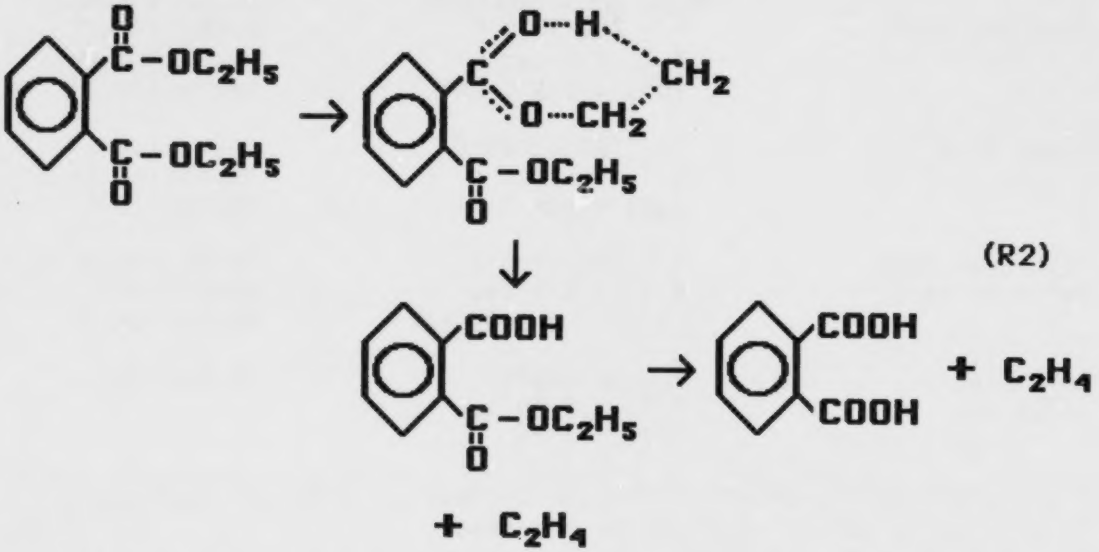
$$\%\text{PIC YIELD} = [\text{PIC}]/[\text{POHC}]_0 \times 100 = 100[1-\exp\{-At \exp(-Ea/RT)\}] \quad \text{(Eqn 1)}$$

where: $[\text{POHC}]_0$ = concentration of parent POHC; [PIC] = concentration of PIC, t = reaction time; A = Arrhenius coefficient for the reaction; Ea = the activation energy for the reaction; T = the reaction temperature; and R = the universal gas constant.

Examples of known concerted molecular elimination include what are referred to as four- and six-center processes. Reaction 1 presents the conversion of pentachloroethane (C_2HCl_5) to tetrachloroethene (C_2Cl_4) and hydrochloric acid (HCl) as an example of a four-center process. Reaction 2 presents the conversion of diethyl phthalate to phthalic acid and ethene (C_2H_4)as an example of a six-center process.[17]



(R1)



(R2)

The former is of particular interest because it illustrates a pathway where a fragile POHC may decompose to form large yields of a thermally stable PIC.[18] The latter is also of interest because it demonstrates how phthalates are easily degraded and should not be observed in incinerator effluents. In light of these degradation pathways, reported observations of phthalate emissions are likely the result of sampling or analytical error or ubiquitous sources, e.g., outgassing of phthalates in plasticizers.[4]

Table 2 presents a list of kinetic parameters for POHCs of interest to incineration that have been experimentally shown to decompose by four- or six-center processes. The reaction rates for these molecules are all energetically favorable under incineration conditions with an extent of reaction greater than 99% at temperatures below 700°C. Because these PIC formation pathways occur so rapidly, the resultant PIC can experience almost the full gas-phase residence time experienced by the parent POHC. Thus, PICs produced by molecular elimination may undergo decomposition resulting in secondary PIC formation, or the reaction may proceed to the formation of thermodynamically stable combustion products.

TABLE 2

EXPERIMENTALLY DOCUMENTED MOLECULAR ELIMINATION PIC FORMATION PATHWAYS

POHC	PIC	MECHANISM	Ea (kcal/mole)	A (1/sec)	T 99 (2)(C)
1,2-Dibromo-3-chloropropane	1-Bromo-2-chloropropene	HBr Elim.	51.3	4.17E13	572
1,1-Dichloroethane	Chloroethene	HCl Elim.	53.5	2.82E13	620
1,2-Dichloroethane	Chloroethene	HCl Elim.	53.5	1.41E13	641
1,1-Dichloropropane	Chloropropene	HCl Elim.	53.5	3.16E13	616
1,2-Dichloropropane	Chloropropene	HCl Elim.	53.7	1.26E13	648
1,3-Dichloropropane	Chloropropene	HCl Elim.	56.6	6.32E13	647
2,2-Dichloropropane	Chloropropene	HCl Elim.	51.5	5.01E13	570
1,2-Dibromoethane	Bromoethene	HBr Elim.	51.3	4.17E13	572
DDT	DDE	HCl Elim.	53.2	7.94E12	654
Diethylphthalate	Phthalic acid	C_2H_4 Elim.	48.0	7.78E12	564
Di-n-butylphthalate	Phthalic acid	C_4H_8 Elim.	46.0	3.08E12	556
Di-n-octylphthalate	Phthalic acid	C_4H_8 Elim.	46.0	3.08E12	556
Pentachloroethane	Tetrachloroethene	HCl Elim.	56.6	5.27E13	652
1,1,1,2-Tetrachloroethane	Trichloroethene	HCl Elim.	56.6	6.32E13	647
1,1,2,2-Tetrachloroethane	Trichloroethene	HCl Elim.	56.6	2.10E13	681
1,1,1-Trichloroethane	Dichloroethene	HCl Elim.	54.0	1.00E14	592
1,1,2-Trichloroethane	Dichloroethene	HCl Elim.	54.0	5.00E13	611
1,2,3-Trichloropropane	Dichloropropene	HCl Elim.	55.0	8.45E13	613

MECHANISM 2: RADICAL-MOLECULE REACTIONS

Examples of bimolecular reactions that result in stable PIC formation are radical-molecule reactions. Once the decomposition of the parent POHC is initiated and a pool of reactive radicals is formed, radical-molecule reactions will usually be the dominant pathway for PIC formation. Hydroxyl (OH) radicals are the dominant reactive species under stoichiometric and oxidative conditions, while H atoms are the dominant reactive species under pyrolytic conditions.[19] In addition, polyatomic organic radicals are also believed to play an important role in the formation of PICs that are of higher molecular weight than the parent compound.

The dominant route for the decomposition of benzene under oxidative conditions has been suggested to involve attack by OH or O

$C_6H_5O\cdot$ may then further decompose to form carbon monoxide (CO) and cyclopentadienyl radical ($C_5H_5\cdot$). $C_5H_5\cdot$ may then react with oxygen to form cyclopentadienonyl radical ($C_5H_5O\cdot$), which will decompose to butadienyl radical ($C_4H_5\cdot$) and CO. Once ring opening has occurred, other stable organic products such as acetylene (C_2H_2) and C_2H_4 may form. This pathway is representative of the oxidation of substituted aromatic species after any side chains or other functional groups have been removed.

Figure 1 depicts the formation of polychlorinated dibenzofurans (PCDFs) from 2,3′,4,4′,5-pentachlorobiphenyl (PCB).[21] A relatively simple mechanism involving OH attack is illustrated in reaction 3. We currently believe that Cl displacement by OH is the first step. This is followed with H abstraction by OH forming the resonance stabilized tetrachlorobiphenoxyl radical. The third step is ring closure forming 2,3,7,8-PCDF. This mechanism occurs with percent yields of products.

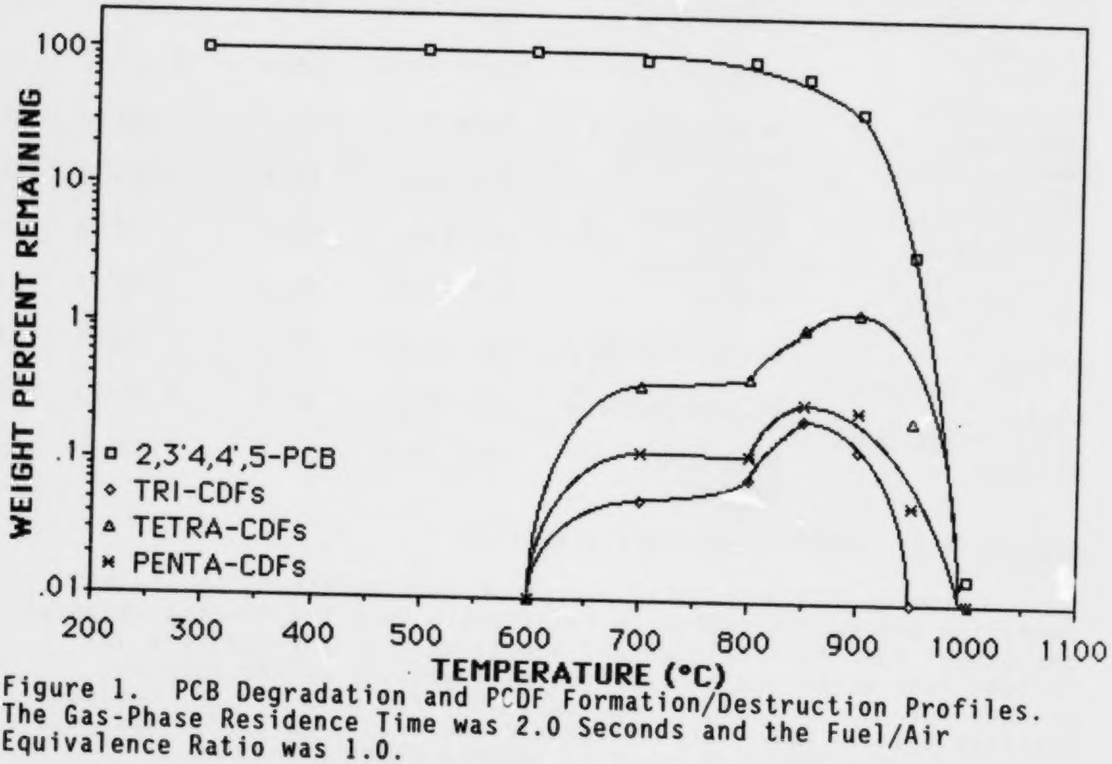


Figure 1. PCB Degradation and PCDF Formation/Destruction Profiles. The Gas-Phase Residence Time was 2.0 Seconds and the Fuel/Air Equivalence Ratio was 1.0.

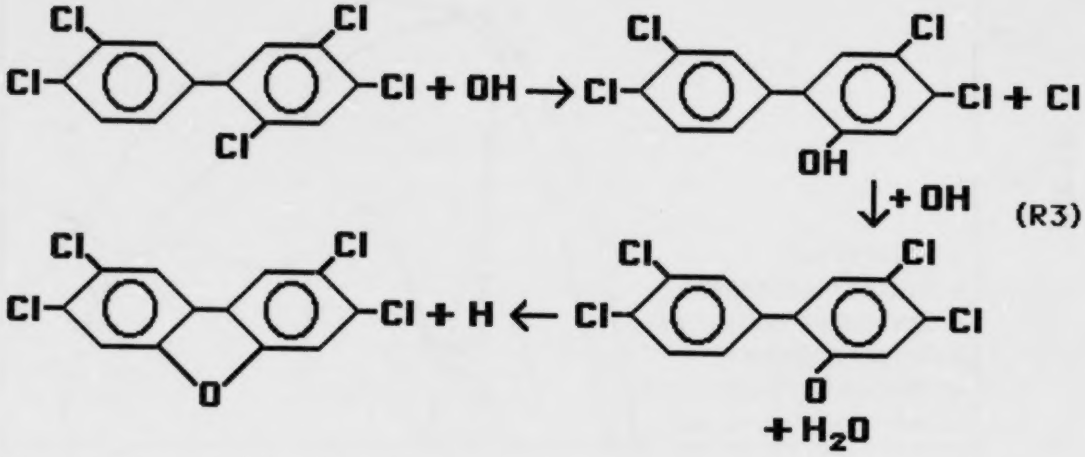


Figure 2 illustrates the formation of a several of the major products from the decomposition of chloroform ($CHCl_3$) under 50% excess air conditions. Of particular interest is the formation of hexachlorobenzene (C_6Cl_6) which is stable at high temperatures and is formed in percent yields. We have previously proposed a mechanism where $CHCl_3$ rapidly forms C_2HCl_5, which decomposes to produce C_2Cl_4 and trichloroethene (C_2HCl_3).[22] A radical-molecule mechanism demonstrating the formation of C_6Cl_6 from C_2HCl_3 through experimentally observed intermediates such as dichloroacetylene (C_2Cl_2) and 1,3-hexachlorobutadiene (C_4Cl_6) is illustrated in reactions 4 through 7.[22]

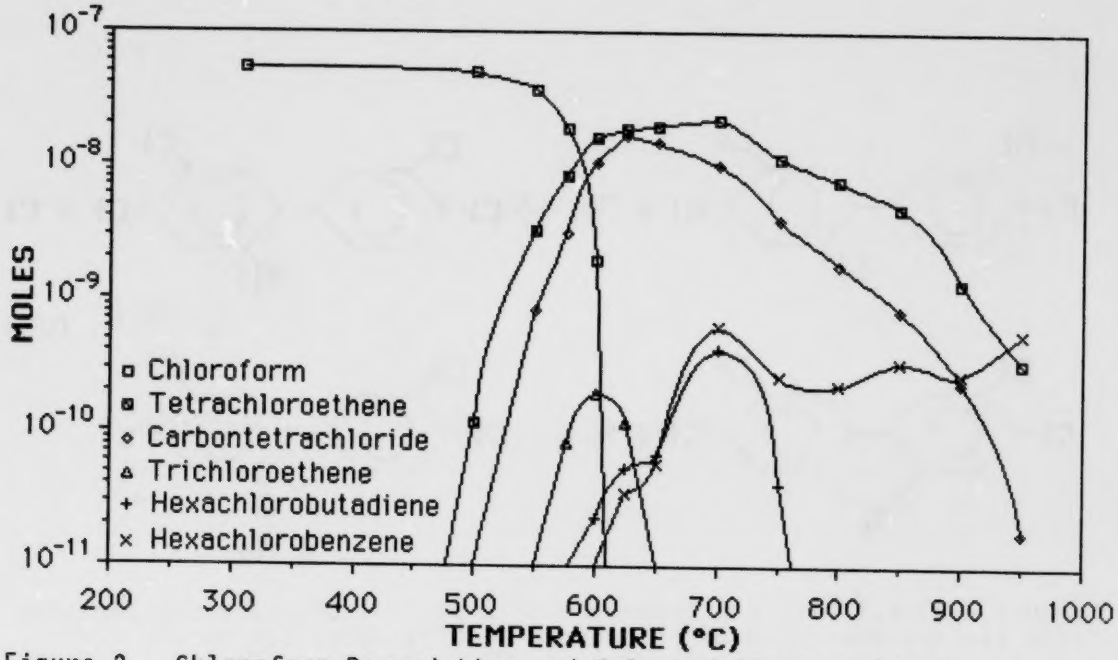
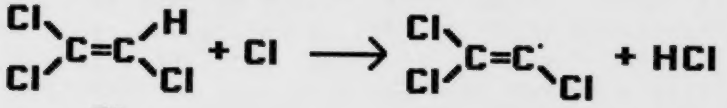
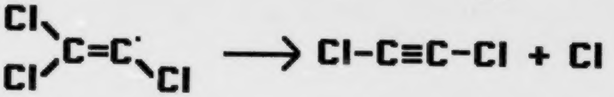
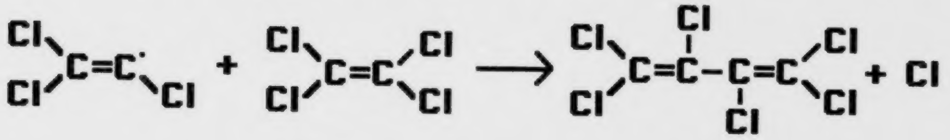
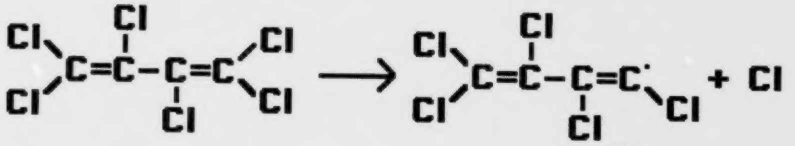


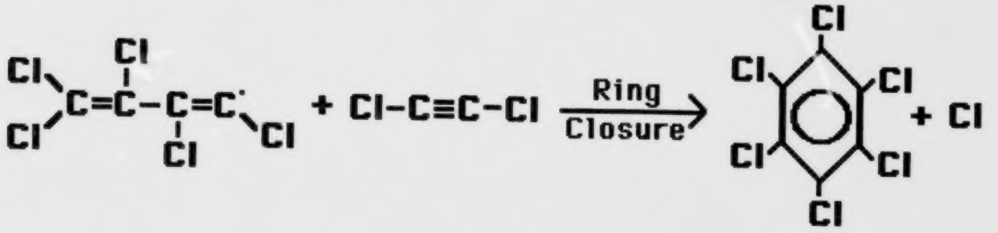
Figure 2. Chloroform Degradation and Selected PIC Formation/ Destruction Profiles. The Gas-Phase Residence Time was 2.0 Seconds and the Fuel/Air Equivalence Ratio was 0.67.


(R4)


(R5)


(R5')


(R6)


(R7)

These examples demonstrate the complexity of the formation of PICs by radical-molecule pathways. It should be recognized that since the rate of PIC formation is dependent on the concentration of both the radical and molecule reaction partners, the observed PIC yield will generally increase with increasing waste feed rate. It is also important to note that many reaction steps may be required for the formation of a given PIC, e.g., C_6Cl_6. Thus, the high-temperature, gas-phase residence time may be very short for such PICs, and their DE be much less than expected based on the full residence time in the incinerator. This is in contrast to PICs formed by concerted molecular elimination and suggests that for identical PIC formation yields for these pathways, the radical-molecule route will result in greater PIC emission rates.

MECHANISM 3: RADICAL-RADICAL RECOMBINATION REACTIONS

Recombination reactions of radicals or atoms to form stable molecules are expected to occur only when molecule concentrations are very low or radical concentrations are high. These reaction rates are second order with respect to radical concentration and are temperature independent or exhibit small negative temperature dependencies. Since radical concentrations in the combustion zone are at least a factor of 100 times less than stable molecule concentrations, it can be shown that the overall forward reaction rate for radical-molecule reactions are typically greater than 50 times the radical-radical reaction rates at temperatures in excess of 1200°C. At lower temperatures, e.g., 800°C, due to the higher activation energy for the radical-molecule reactions, the ratio of rates decreases to ~10. As an example, these results were obtained by evaluating the following equation which compares relative reaction rates for recombination of trichloromethyl ($CCl_3\cdot$) radicals and Cl atoms versus displacement of a Cl atoms from C_2Cl_4 by $CCl_3\cdot$:

$$\frac{\text{Rate of Displacement}}{\text{Rate of Recombination}} = \frac{A'\exp(-Ea'/RT)[C_2Cl_4][CCl_3]}{A\exp(-Ea/RT)\,[Cl][CCl_3]} \qquad \text{(Eqn 2)}$$

Since product distributions are exponentially dependent on the reaction rate, radical-molecule reactions are clearly kinetically favored routes as compared to recombination reactions at temperatures greater than 600°C.

Since chemical reaction kinetics in the high-temperature and post-flame zones of incinerators are extremely rapid, thermodynamic equilibrium codes can be used to predict with reasonable accuracy the free radical concentrations at these temperatures.[23] Thus, radicals with small (or negative) free energies for overall reaction pathways (ΔGrxn) may be expected to be present in significant concentrations, i.e, thermodynamically stable, and exit the flame zone. Table 3 lists a large number of radicals that may form in hazardous waste incinerators along with their free energies (ΔGf) and heats of formation (ΔHf). The heat of formation of these radicals may be used along with the heat of formation of possible dissociation products (ΔHdiss) to calculate the energy required for β bond homolysis, which represents an alternative pathway for destruction of the radicals. The lower the values of ΔGrxn and the higher the values of ΔHdiss, the more likely these species will exit the flame zone of an incinerator.

Once in the cool zone, temperatures may be sufficiently low that radical-molecule reactions with stable combustion endproducts now present in high concentrations, e.g., CO_2, H_2O, and HCl, occur at a much slower rate. As a result, radical-radical recombination routes may now become kinetically significant. If the temperature is rapidly quenched downstream of the post-flame zone, the concentrations of these radicals may be predicted from equilibrium calculations at the temperature just upstream of the quenching boundary. With this information, the recombination product concentrations downstream of the quenching boundary can be generally related to the predicted radical concentrations. Once formed, these molecules are not subjected to high temperatures and may exit the incinerator undestroyed.

TABLE 3

THERMODYNAMIC PROPERTIES OF SELECTED RADICALS PRODUCED IN HAZARDOUS WASTE INCINERATION

SPECIES	ΔHf (300 K) (kcal/mole)	ΔGf (1000 K) (kcal/mole)	REFERENCE
H	52.103	39.562	24
OH	9.432	5.706	24
HO_2	4.996	16.021	24
O	59.562	44.875	24
F	18.863	4.522	24
FO	26.000	22.884	24
CFO	-41.000	-50.043	24
CF_2	-43.501	-50.947	24
CF_3	-112.403	-101.283	24
Cl	28.924	15.547	24
ClO	24.192	21.123	24
CClO	-15.000	-26.205	24
CCl_2	57.000	48.001	24
CCl_3	19.002	28.838	24
$CHCl_2$	24.058	27.807	16
CH_2Cl	28.260	30.807	16
CH_3	34.814	38.179	24
C_2F_5	-213.000	-171.048	16
C_2Cl_5	8.897	48.535	16
C_2HCl_4	5.387	40.618	16
$C_2H_2Cl_3$	11.800	45.032	16
C_2H_5	26.500	53.593	16
C_2Cl_3	53.000	55.363	16
C_2HCl_2	52.000	54.153	16
C_2H_3	69.000	64.452	16
C_3H_5	40.600	64.112	16
n-C_3H_7	21.000	71.157	16
i-C_3H_7	17.600	69.693	16
C_6H_5	70.043	87.593	25
C_7H_7	45.000	93.430	16

SUMMARY

We have discussed how three fundamentally different mechanisms for gas-phase formation of PICs can occur in a hazardous waste incinerator. These mechanisms are: 1) concerted molecular elimination reactions, 2) radical-molecule reactions, and 3) radical-atom or radical-radical recombination reactions.

Concerted molecular elimination occurs very early in the incinerator and produces mostly olefinic species. Radical-molecule routes also occur in this region and extend further into the high-temperature flame and post-flame zone. Radical-molecule reactions can lead to fragmentation of POHCs to form lower molecular weight PICs or form higher molecular weight PICs by radical chain mechanisms. Relatively slow recombination reactions involving stable radicals are likely to occur in the cooler downstream regions of the incinerator and tend to result in the formation of highly fluorinated and chlorinated alkanes. As a result of their formation in successively downstream regions, PICs produced by recombination reactions experience a concomitant decrease in their high-temperature, gas-phase residence times. Since the ultimate yield of PICs in the effluent depends on both the extent of formation and the extent of destruction, PICs formed in the cooler zones may exhibit greater emission rates. However, the reactivity of each PIC will be a major factor and much uncertainty still exists over which reaction class results in the greatest emissions.

We are continuing our experimental studies of each reaction class and the factors affecting their reaction rates. We are combining these studies with kinetic and thermodynamic computations to provide subroutines that may be included in scale-up models of incinerators.

ACKNOWLEDGMENTS

This research was partially supported by the US-EPA under cooperative agreement CR-813938.

LITERATURE CITED

1. Oppelt, E. T., APCA Journal, 37, 1987, pp. 558-586.

2. Lee, K. C., APCA Journal, 37, 1987, pp. 1011-1017.

3. Dellinger, B., "Theory and Practice of the Development of a Practical Index of Hazardous Waste Incinerability," Hazard Assessment of Chemicals-Current Developments, J. Saxenor, ed., in press.

4. Midwest Research Institute, "Performance Evaluation of Full-scale Incinerators," US-EPA HWERL Report, EPA-600/2-84-181, 1984.

5. Castaldini, C., et al., Haz. Waste Haz. Mat., 1, 1984, pp. 159-165.

6. EPA Science Advisory Board, "Report on the Incineration of Liquid Hazardous Waste by the Environmental Effects, Transport, and Fate Committee," April 1984.

7. Hershkowitz, A., Technol. Review, July 26, 1987.

8. Dellinger, B., et al., Haz. Waste Haz. Mat., 3, 1986, pp. 139-152.

9. Dellinger, B., et al., Haz. Waste Haz. Mat., 3, 1986, pp. 293-307.

10. Tsang, W., "Fundamental Aspects of Key Issues on Hazardous Waste Incineration," to be published.

11. Taylor, P. H. and Dellinger, B., "A Thermal Stability Based Ranking of Hazardous Organic Compound Incinerability," Proceedings of the International Symposium on Incineration of Hazardous, Municipal, and other Wastes, Palm Springs, CA 1987.

12. Dellinger, B., et al., "Products of Incomplete Combustion from the High-Temperature Pyrolysis of Chlorinated Methanes," to be presented at the 195th National Meeting of the American Chemical Society, Toronto, Ontario, Canada, June 1988.

13. 40 CFR, Part 261, Appendix VIII, pp. 373-378.

14. Rubey, W. A. and Carnes, R. A., Rev. Sci. Instrum., 56, 1985, pp. 1795-1798.

15. Rubey, W. A., "Design Characteristics of the Thermal Decomposition Analytical System," US-EPA HWERL Report, EPA-600/2-80-098, 1980.

16. Benson, S. W., Thermochemical Kinetics, 2nd ed., John Wiley, New York, 1976.

17. Benson S. W. and O'Neal, H. E., "Kinetic Data on Gas-Phase Unimolecular Reactions," NSRDS-NBS 21, National Bureau of Standards, Washington, D.C., 1970.

18. Dellinger, B., et al., Haz. Waste Haz. Mat., 1, No. 2, 1984, pp. 137-157.

19. Tsang, W., "High-Temperature Chemical and Thermal Stability of Chlorinated Benzenes," Proceedings of the International Symposium on Incineration of Hazardous, Municipal, and other Wastes, Palm Springs, CA 1987.

20. Brezinsky, K., Prog. Energy Combust. Sci., 12, 1986, pp. 1-24.

21. Rubey, W. A., et al., Chemosphere, 14, No. 10, 1985, pp. 1483-1494.

22. Taylor, P. H. and Dellinger,B., "Thermal Degradation Characteristics of Chloromethane Mixtures," Environ. Sci. Technol., Vol. 22, No. 4, p. 438, 1988.

23. Reynolds, W. C., "STANJAN Equilibrium Program, Version 3.0," Department of Mechanical Engineering, Stanford University, Stanford, CA, 1986.

24. Stull, D. R. and Prophet, H., JANAF Thermochemical Tables, 2nd Edition, NSRDS-NBS 37, National Bureau of Standards, Washington, D.C., 1971.

25. Bahn, G. S., "Approximate Thermochemical Tables for Some C-H abd C-H-O Species," NASA CR-2178, 1973.

"Studies of POHC DE During Simulated Atomization Failure in a Turbulent Flame Reactor"

by

Daniel P.Y. Chang
Professor and Visiting Research Engineer
Department of Civil Engineering
University of California, Davis

Marta K. Richards, Research Chemist

and

George L. Huffman, Chief
Thermal Processes Research Staff
Thermal Destruction Branch
U.S. EPA Hazardous Waste Engineering Research Laboratory

ABSTRACT

The failure of flames to destroy waste molecules determines the residual amounts of POHCs and PICs that have to be destroyed by subsequent thermal reactions in the post-flame zone of a combustor. Oversized "rogue droplets" have been suggested as one means by which POHCs escape a flame. This paper presents results of POHC destruction efficiency (DE) experiments under conditions of a simulated atomization failure leading to the generation of oversize droplets.

Four pairs of POHCs were burned with heptane in a turbulent flame reactor (TFR) at constant H:Cl ratio under a simulated condition of atomization failure. Compound DE was measured principally by GC/FID. Differences in compound DE were observed and relative DE of each pair of POHCs was determined. The observed order of incinerability from most to least difficult was 1,2,4-trichloro-benzene (TCB) > tetrachloroethene (PERC) > trichloroethene (TCE) > 1,1,2,2-tetrachloroethane (TCA) >> 1-chloropentane (CP) and heptane (HEPT). Such a ranking is consistent with limited burning-rate and low oxygen thermal stability data, and with theoretical flame mode kinetics reasoning. Some PICs (benzene, chlorobenzene, TCE, toluene) were found to increase with increasing CO concentration for the particular failure condition examined, while others appeared to be present at a more or less constant background level.

INTRODUCTION

Waste incineration has been conceptualized as a two-stage process. In the flame-zone, near adiabatic flame temperatures, extremely rapid reactions, and high concentrations of reactive species characteristic of flames, convert reactants introduced with the fuel/waste mixture on relatively short time scales (< 0.1 s). In the post-flame, high-temperature, thermal decomposition zone (characterized by slower reaction rates, lower concentrations of reactive species, but residence times on the order of seconds), appreciable conversion of reactants persists. A possible explanation for the escape of some reactants from the flame-zone can be attributed to the "rogue droplet" hypothesis (Mulholland, 1987), in which an oversize particle of fuel/waste passes out of the flame-zone before completely evaporating. In such a circumstance, the oversize droplet could behave as an isolated burning droplet. It is known that individual droplets which have been ignited in the flame-zone will eventually extinguish in a cooler post-flame environment before complete consumption of the reactants (Law, 1975). In such a case, only one out of a multitude of droplets need escape the flame to account for the low levels of residual organic substances emissions (ROSE) observed in poorly operated incinerators.[1]

If the conceptual models described above are reasonably accurate, then a flame-based ranking scale founded on droplet burning characteristics (burning-rate and/or flame extinction), might be developed to complement the University of Dayton Research Institute's (UDRI) gas-phase thermal stability (TS) ranking (Dellinger, 1985a). The logic in applying such rankings would be that those compounds highly ranked on both scales would be difficult to destroy in liquid-injection incinerators. Therefore they would be suitable candidates for surrogate compounds to be used in testing the ability of an incinerator to destroy the principal hazardous organic constituents (POHC) of a waste.

In liquid-injection incinerators, sprays are typically generated, and burning occurs at the periphery of evaporating clouds of droplets. This occurs because of rate limitations on the mixing of oxidant into the cloud. A major question to be addressed as part of the current project was whether any of the results of single droplet burning experiments could be related to spray combustion when oversize droplets, a simulated "failure-mode", were purposely introduced into a turbulent diffusion flame. This paper deals with an experimental study of oversize droplets burning in a turbulent flame reactor (TFR) located at the U.S. EPA's Center Hill Laboratory (Staley *et al.*, 1986) and concommitant development of sampling and analytical methods in support of those experiments.

---

[1] The term residual organic substance emission (ROSE) is being used in this paper to refer to those organic compounds which are in the feed, *e.g.* POHCs, but not completely destroyed by the combustion process, those compounds which are possibly reformed or newly formed in the incinerator (not limited to the USEPA definition of product of incomplete combustion, PIC, which requires appearance in "Appendix VIII"), and those compounds which represent products other than inorganic combustion products such as CO, CO_2, H_2O, HCl, or Cl_2.

DESCRIPTION OF RESEARCH CONDUCTED

The research program consisted of two phases: 1) preliminary development of a sampling methodology for simultaneous collection of volatile and semi-volatile organic compounds using multi-sorbent traps (TAC - TENAX-TA^R, Ambersorb^R, charcoal); 2) relative destruction efficiency (DE) tests of four pairs of chlorinated hydrocarbons (CHC) blended with heptane (HEPT) under simulated atomization failure conditions (oversize droplets).

Semi-volatile organic compounds (SVO) were of interest in this study because data on single droplet burning were available only for compounds whose boiling points were greater than 90 ^oC. Volatile organic compounds (VOC) were also of interest because previous work carried out on the TFR had concentrated on VOCs. For reasons of equipment costs, data comparability and physical limitations imposed by a thermal desorption unit interfaced to the analytical equipment (Envirochem^R UNACON 810A), it was desirable that 6 mm o.d. X 4 mm i.d. X 203 mm long glass tubes be used to house the sorbent traps. Two additional constraining problems had to be overcome: one was the transmission of higher boiling compounds through the sampling line, and the second was the avoidance of water vapor condensation in the sorbent traps. These problems were addressed by maintaining the sampling line (see Figure 1) and a commercially available multi-sorbent TAC trap at higher temperatures (150 to 160 ^oC and 74 ^oC, respectively) than is specified for the volatile organic sampling train (VOST). A preliminary validation of the sampling method was undertaken for purposes of this research project. This consisted of retention and recovery experiments using known quantities of standards "spiked" onto the sorbent tubes and subsequently analyzed by GC/FID.

Five compounds 1-chloropentane (CP), 1,1,2,2-tetrachloroethane (TECA), trichloroethene (TCE), tetrachloroethene (PERC) and 1,2,4-trichlorobenzene (TCB) were selected for this study. These were burned as pairs in the TFR to determine relative DE. Previous work with the TFR (Kramlich *et al.*, 1985) had demonstrated that oversize droplets could be produced by simply re-

DIAGRAM of TAC SAMPLING LINE for VOC & SVOCs

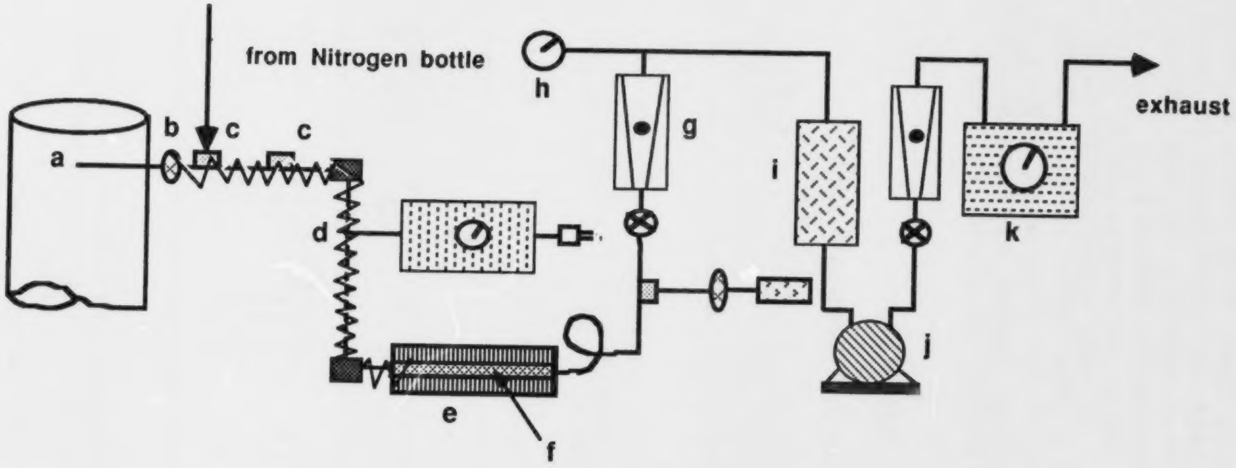


Figure 1: TAC Sampling System. (a) 6 mm o.d. quartz probe tip into which a plug of glass wool was inserted; (b) Teflon/stainless steel sample line isolation valve; (c) stainless steel "tees" for standard spike injection or nitrogen purge; (d) heated, temperature-controlled 6.35 mm (1/4 in.). o.d. stainless steel tube sampling line 150 to 160 °C; (e) heated, temperature-controlled (74°C) aluminum block which contained the sorbent trap; (f) Envirochem® (TAC) sorbent tube, 204 mm long X 6 mm o.d. X 4 mm i.d.; (g) rotameter equipped with a needle valve for flow control; (h) vacuum gauge; (i) silica gel drying column; (j) airtight sample pump; (k) one liter per revolution dry gas meter.

ducing the pressure supplied to the atomizing nozzle. Thus a 1.5 gph, Delevan^R WDA 60° hollow-cone nozzle operated at 40 psig was used to produce the oversize droplets. In order to maintain the thermal environment in the TFR as close to the same as possible, identical fuel feed rate, stoichiometry and turbulent mixing (swirl setting) were used in each run. To reduce variability in stoichiometry, it was decided to concoct the mixtures such that equimolar amounts of each POHC would be blended with heptane to yield an overall H:Cl ratio of 100:1 (about 5.3 weight % Cl). It was undesirable that a primary decomposition product of a POHC also be one of the POHCs in a mixture, therefore, mixtures of TECA with TCE were avoided since TCE was a known decomposition product of TECA. The composition of the "cocktails" is shown in Table 1.

Table 1

POHC Mixture Compositions

Compound		b.p. [°C]	M.W.
CP	chloropentane	107.8	106.6
TECA	1,1,2,2-tetrachloroethane	146.0	167.9
TCB	1,2,4-trichlorobenzene	231.5	181.5
PERC	tetrachloroethene	121.0	165.8
TCE	trichloroethene	87.0	131.4
HEPT	heptane (technical grade)	98.4	100.2

Mixture	average composition C	H	Cl	Cl conc. wt. %
CP:TECA:HEPT	1.00	2.27	0.023	5.3%
TECA:TCB:HEPT	1.00	2.24	0.022	5.3%
PERC:TCB:HEPT	1.00	2.24	0.022	5.3%
TCE:TCB:HEPT	1.00	2.23	0.022	5.3%

Two sorbent tube samples were also analyzed by mass spectrometry (GC/MS) on a chromatograph equipped with an identical analytical column (J & W Scientific, DB-1, 30 m X 0.32 mm i.d., stationary phase cross-linked and bonded, fused silica capillary column) to the GC/FID used for DE tests. By careful matching of identified peaks and retention times, certain ROSEs were also tentatively identified and quantified retrospectively. These are listed in Table 2. Further details regarding experimental procedures are given by Chang *et al.* (1988).

Table 2

Boiling Point and Retention Times

Compound	b.p. °C	Combined data MS [s]	 FID [s]
dichloromethane (DCM)	40.5	313	265
Freon 113 (F113)	47.7	330	
1-hexene	63.4	452	
chloroform ($CHCl_3$)	61.2	485	447
1,2-dichloroethane (EDC)	84.0	546	
1-chlorobutane	78.4	577	
benzene (BZ)	80.1	608	557
CCl_4 (CARB TET)	76.8	624	569
2-methylhexane	90.0	668	
pentanal	103.0	686	639
3-methylhexane	92.0	692	
trichloroethene (TCE)	87.0	717	662
heptane (HEPT)	98.4	762	712
methylcyclohexane	100.4	816	
1-chloropentane (CP)		879	832
toluene (TOL)	110.6	916	863
hexanal	128.0	987	937
3-methyleneheptane		1017	
4-octene (identity?)	122.0	1022	971
tetrachloroethene (PERC)	121.0	1048	986
4-octene (identity?)	122.0	1066	1015
chlorobenzene (ClBZ)	132.0	1132	1069
1-chlorohexane	134.5	1175	1132
tetrachloroethane (TECA)	146.0	1275	1215
nonane	150.8	1337	
bromofluorobenzene (BFB)	152.0	1338	1278
benzaldehyde	178.1	1410	
benzofuran	174.0	1534	
1,4-dichlorobenzene	174.0	1559	
nonanol	212.0	1565	
1,2-dichlorobenzene	179.0	1572	
1-decene	170.6	1588	
1-chlorononane	203.0	1713	
3,7-dimethyloctanol	212.0	1808	
1,2,4-trichlorobenzene	231.5	1973	1895
1-chlorodecane	223.4	2185	2110
1-bromodecane	240.6	2349	
tetradecane	253.7	2470	2422
5,7-dimethylundecane		2832	
2,3,6-trimethyldecane		2833	

RESULTS OF TAC SORBENT TUBE RETENTION AND RECOVERY STUDY

A triplicate set of tubes, to which known amounts of standards had been delivered, was exposed to two liters of combustion gases from the TFR while technical grade heptane was being burned. The tubes were subsequently analyzed for the amount of each POHC remaining and compared to identically "spiked" tubes which had not been exposed. It was assumed that the internal standard recovery, bromofluorobenzene (BFB), was 100% in each case, and the other compound recoveries were normalized to the amount of BFB recovered. The results are shown in Table 3 (column labelled "retention efficiency"). The results clearly indicate that considerable loss of dichloromethane, carbon tetrachloride, and trichloroethene occurred at the 74 ^{0}C test condition.

Table 3

Retention and Recovery Efficiency Results

Standard	Retention efficiency	std. dev.	Recovery efficiency	std. dev.
DCM	19%	13%	27%	14%
CCl4	54%	9%	125%*	24%
TCE	41%	15%	50%	13%
HEPT	107%	17%	116%	10%
CP	107%	16%	112%	9%
PERC	65%	19%	71%	9%
CLBZ	103%	16%	105%	8%
TECA	79%	16%	82%	6%
TCB	105%	20%	91%	16%
BFB	100%	n.a.	100%	n.a.

*benzene interference
n.a. = not applicable

The results of "spiking" known quantities of the standards in methanol solution at the head of the sampling line are also shown in Table 3 (column labelled "recovery efficiency"). In this case the "spike" was evaporated into two liters of TFR combustion gas which was passed through the TAC sorbent tube. Slightly higher recoveries of the "spiked" compounds were noted. In the oversize droplet POHC DE studies described below, DEs were corrected for recovery efficiencies shown in Table 3.

The above assessment of the TAC tubes and sampling line indicated that while operation at elevated temperatures ensured transmission of the POHCs of interest, SVOs, and prevention of water vapor/HCl condensation, recovery of VOCs normally trapped by the VOST methodology was less than desired. However, the multi-sorbent tubes did extend the range of compounds that could be successfully captured on a single trap to both VOCs and some SVOs. SVOs could be quantified and qualitative data on VOCs could be obtained simultaneously.

OVERSIZE DROPLET RESULTS AND DISCUSSION

Clear differences in the DE of the fuel/POHC cocktails were observed. The differences were smaller for the most refractory compounds TCB and PERC, but were several orders-of-magnitude between the most and least refractory POHCs tested, TCB and CP, respectively. A relative ranking of compounds was constructed from the observed absolute penetrations (Pt = 1 - DE) by normalizing to the TCB penetration. No physical significance should be attached to the numerical values of the relative Pt reported. The ranking is shown in Table 4 along with a ranking based on heat-of-combustion (Hc), gas phase thermal stability under high O_2 ($TSHiO_2$) and low O_2 ($TSLoO_2$), and lastly theoretical flame mode kinetics (TFMK) under low O_2 conditions. The actual DEs observed for one control test (TCE:TCB:HEPT) with nominally optimum droplet atomization and for oversize droplets is also shown for comparison in Table 5.

The results of the oversize droplet DE study suggest that a relatively small number of chlorine atoms in comparison to the hydrogen atoms, 1:100 (5.3% Cl by weight), can produce noticeable effects on the combustion process as evidenced by increased CO production (several hundred ppm above heptane alone - see Figure 2). This difference in CO production is believed to have resulted primarily from chemical effects since the reduced specific energy of the POHC/heptane mixtures resulted in overall exhaust temperature decreases of only 10 to 15 ^{o}C, while the change in theoretical adiabatic flame temperature, assuming the same amount of air supplied to the POHC/fuel mix as for fuel alone, was also calculated to be less than about 35 ^{o}C.

ASSESSMENT OF RESIDUAL ORGANIC SUBSTANCE EMISSIONS

Complete identification of all emissions was not the primary goal of the project. However using a retention time correlation constructed from comparison of GC/FID and GC/MS analyses it was possible to tentatively identify some peaks observed in the chromatograms. The concentrations of selected products of incomplete combustion (PIC), tabulated as GC/FID area of the PIC normalized by area of the internal standard (BFB), is shown in Table 6.

Table 4

Comparison of POHC DE with Various Ranking Methods

Compound	Relative Penetration	Drop	Rank based upon: Hc*	TSHiO$_2$*	TSLoO$_2$*	TFMKLoO$_2$
TCB	1.0E+00	1	4 (64/272)	3 (12/23)	1 (1/43)	1
PERC	6.0E-01	2	1 (11/272)	1 (2/23)	2	2
TCE	3.8E-01	3	3 (22/272)	2 (9/23)	3	3
TECA	7.6E-02	4	2 (16/272)	4 (21/23)*	4 (6/43)*	4
CP	9.3E-04	5	5 (NA)	NA (NA)	NA (NA)	5
HEPT	5.2E-04	6	6	NA	NA	6

* Values in parentheses are the ranks reported in the reference sources used except for 1,1,2,2-TECA for which it was assumed 1,1,1-trichloroethane would give similar ranking.

Hc - (CARB, 1986)
TsHiO2 - (Dellinger, 1984) observed T_{99}
TsLoO2 - (Taylor, 1987)
TFMKLoO2 - (Tsang and Shaub, 1982; Tsang, 1987)

Table 5

Comparison of TCE:TCB:HEPT Penetration for Optimum and Oversize Droplets

	Penetration Optimum	Oversize
TCE	6.2E-06	1.4E-04
TCB	8.8E-06	4.1E-03
HEPT	5.9E-08	2.6E-07

When burning TECA-containing mixtures, a chromatographic peak assigned to TCE was clearly present. The ratio of TCE to TECA in those cases ranged from about 1.5 to 2.5. TCE concentrations were observed at levels about an order-of-magnitude lower when TCE was a POHC in the mixture and TECA was absent.

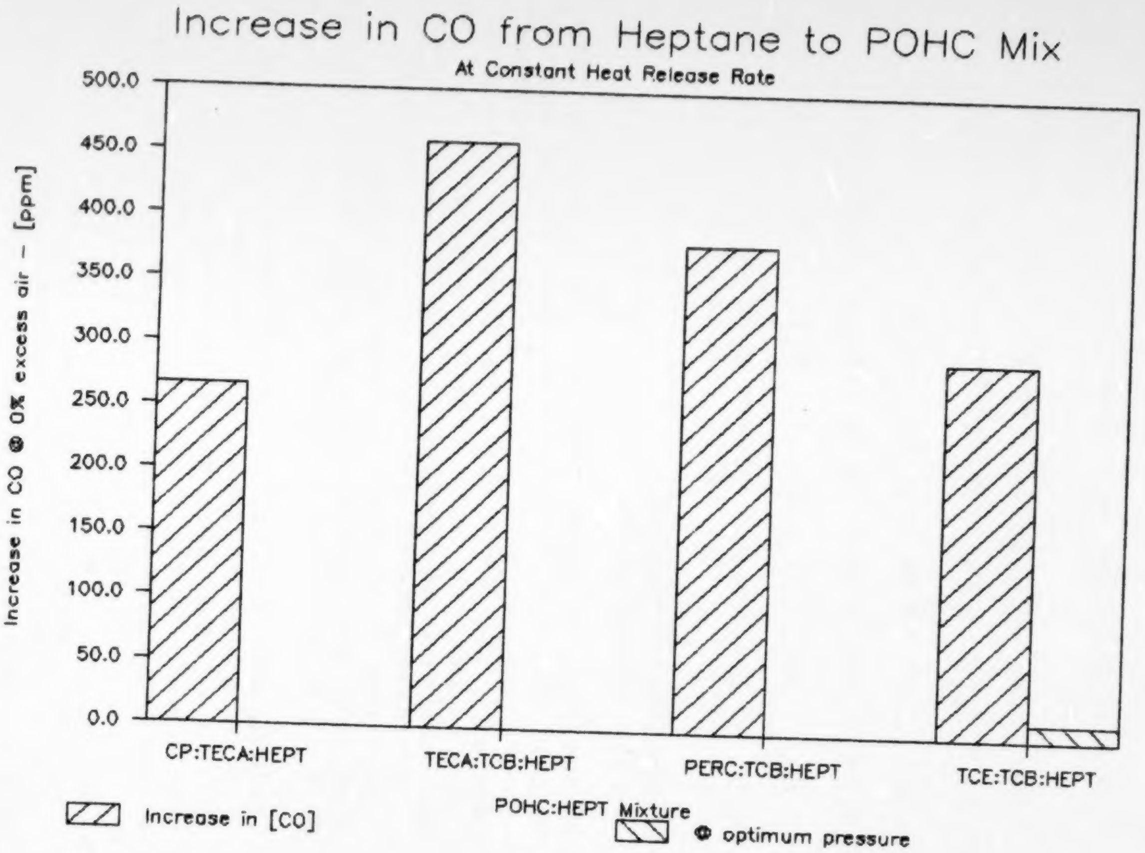


Figure 2. Increase in CO emission when switching from heptane alone to POHC: heptane mixtures for four mixtures under poor atomization conditions. Also comparing result to increase in CO emissions for one POHC: heptane mixture under optimum atomization conditions.

Formation of PICs that are specific to certain POHCs does appear to occur in the oversize droplet model.

Table 6

Selected PIC Summary

GC/FID Relative Area Count

POHC Mix	DCM	$CHCl_3$	EDC	BZ + CARB TET**	TCE	TOL	ClBZ
CP:TECA:HEPT	0.61	0.86	0.55	44.63	2.52	0.62	1.29
TECA:TCB:HEPT	0.14	0.36	0.33	22.91	1.41	0.33	1.09
PERC:TCB:HEPT	0.12	1.36	0.35	14.20	0.15	0.28	0.78
TCE:TCB:HEPT	NA	NA	NA	21.29	0.33	NA	1.37
HEPT*	0.04	0.67	0.44	3.26	0.04	0.17	N.D.
TCE:TCB:HEPT*	0.05	0.87	0.42	2.68	0.02	0.26	N.D.

*Optimum nozzle atomization pressure

**Believed to be primarily benzene

Benzene was observed in every POHC mix and in the heptane-only sample. Benzene was apparently formed from one or more of the components of the fuel, possibly one of the cyclic alkanes present in abundance in the technical grade heptane. Whenever substantial amounts of benzene were formed, a smaller amount of chlorobenzene was observed, independent of the POHCs contained in the mixture. No chlorobenzene was observed when burning heptane alone. This was interpreted to mean that common recombination chemistry was also occurring, *e.g.*, substitution of a hydrogen atom on a ring by a chlorine atom.

With the limited data available, concentrations of PICs were compared with CO concentrations. A consistent relationship was observed for CO and benzene and is shown in Figure 3. This suggests that the residual levels of CO and benzene observed in the exhaust gases were related through a common physical mechanism, *i.e.*, poor atomization, in conjunction with a common chemical mechanism, *i.e.*, interference of CO oxidation by chlorinated species. Note that the POHC mixture (CP:TECA:HEPT) that yielded the highest benzene level was not the most difficult to destroy, but rather, relatively the easiest.

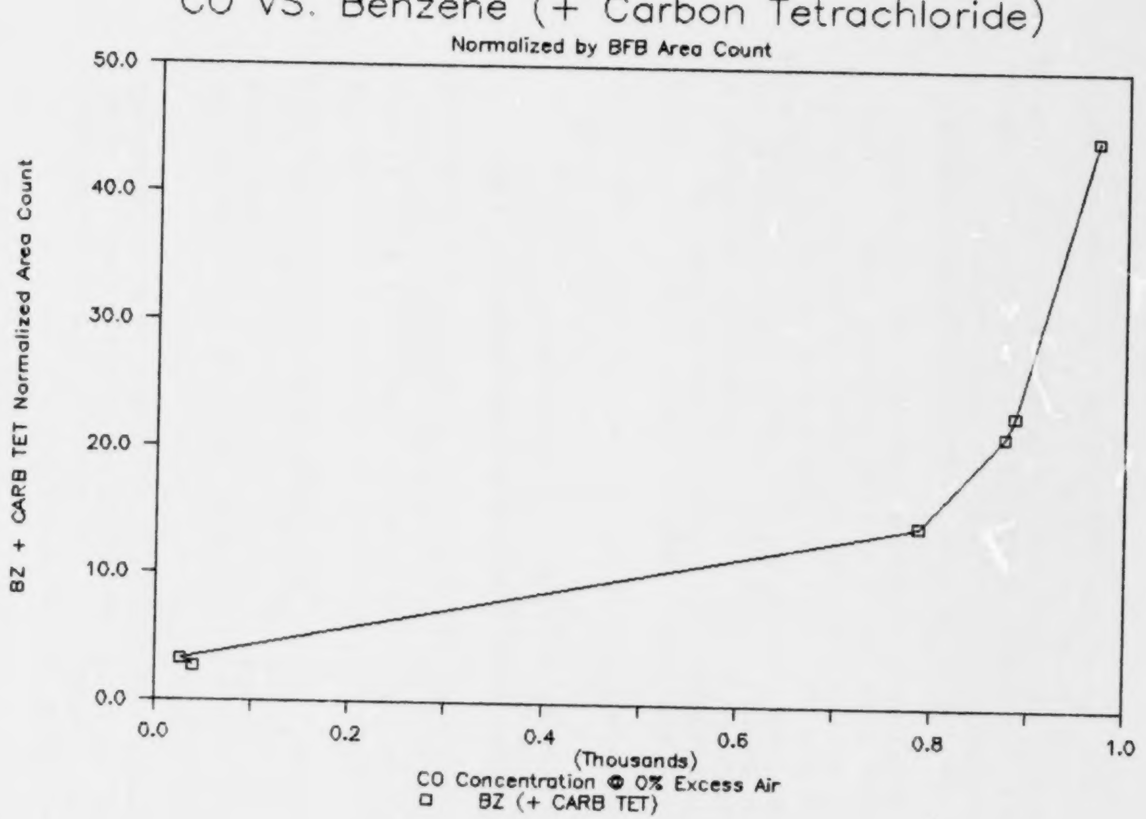


Figure 3. Observed benzene emissions as a function of CO concentration at 0% excess air for four POHC mixtures with poor atomization, heptane alone and one POHC/heptane mixture at optimum atomization.

CONCLUSIONS

The following statements can be made on the basis of the experiments presented in this paper (additional details are presented in the parent reports, Chang *et al.*, 1988; Sorbo *et al.*, 1988):

1) The oversize droplet model, in a water-wall-quenched TFR, provides a consistent picture of incomplete combustion of large fuel/POHC droplets. Flame-extinction phenomena observed in single droplet combustion experiments and the "rogue droplet" hypothesis are consistent with the observations. However, the observations made are not conclusive.

2) The destruction efficiency of five POHCs was established with the oversize droplet model. The resulting ranking agreed with both gas-phase thermal stability and theoretical flame-mode kinetics rankings under low oxygen conditions. This was true even though an overall fuel-lean stoichiometry prevailed in the combustion unit under conditions of moderate turbulent mixing. The order of difficulty of destruction was TCB > PERC > TCE > TECA > CP > HEPT.

3) Given close attention to reproducing combustion conditions as nearly as possible, increases in CO level were apparent when simulating a "failure condition" given relatively small additions of chlorine (5% by weight) into a hydrocarbon fuel.

4) Evidence was obtained for a relationship between CO and benzene emissions for the specific failure condition of oversize droplets combined with flame-quenching under conditions of optimum stoichiometry.

5) Although the CP/TECA/HEPT mixture exhibited the highest DE of the two POHCs in the mixture, it also yielded the highest levels of the PIC benzene under conditions of constant heat release rate and overall stoichiometry.

6) Evidence for POHC-specific and POHC-independent formation of PICs was obtained. TCE produced from TCA was an example of the former, and chlorobenzene was an example of the latter.

REFERENCES

Chang, D.P.Y., Richards, M.K. and Huffman, G.L. "Spray Combustion Studies of Surrogate Hazardous Waste Incineration." Draft Final Report for U.S. EPA Cooperative Research Agreement No. CR-813333-01-1, 1988.

Dellinger, B., Torres, J.L., Rubey, W.A., Hall, D.L., Graham, J.L. "Determination of the Thermal Decomposition Properties of 20 Selected Hazardous Organic Compounds." EPA-600/S2-84-138, 1984.

Dellinger, B., Graham, J., Hall, D. and Rubey, W. "Examination of Fundamental Incinerability Indices for Hazardous Waste Destruction." In: Incineration and Treatment of Hazardous Waste EPA/600/9-85/028, September, 1985a, p.160.

Dellinger, B., *et al.* "PIC Formation Under Pyrolytic and Air Starved Conditions." Report on Grant No. CR 81-0783-01 to the US EPA Hazardous Waste Engineering Research Laboratory, Cincinnati, OH., 1985b.

Kramlich, J., Poncelet, E., Seeker, W.R. and Samuelsen, G.S. "A Laboratory Study on the Effect of Atomization on Destruction and Removal Efficiency for Liquid Hazardous Waste." In: Incineration and Treatment of Hazardous Waste, EPA/600/9-85/028, September, 1985. p.182.

Law, C.K. "Asymptotic Theory for Ignition and Extinction in Droplet Burning." Combustion and Flame, 24:89-98, 1975.

Mulholland, J.A. "Influence of Atomization Parameters on Droplet Stream Trajectory and Incineration." In: Land Disposal, Remedial Action, Incineration and Treatment of Hazardous Waste, EPA-/600/9-87/015, 1987. p.246.

Sorbo, N., Chang, D.P.Y., Steeper, R.R. and Law, C.K. "Engineering Evaluation and Control of Toxic Airborne Effluents Part I: Single Droplet Studies of Surrogate Hazardous Waste Incineration." Draft Final Report, California Air Resources Board Contract #A6-051-32, 1988.

Staley, L.J., Richards, M.K., Huffman, G.L. and Chang, D.P.Y. "Incinerator Operating Parameters That Correlate With Performance." U.S. EPA Final Report on Project D109/T/38/02/3435[A] Workplan #01269a, Hazardous Waste Engineering Research Laboratory, Cincinnati, OH, June, 1986.

Taylor, P.H. and Dellinger, B. "A Thermal Stability Based Ranking of Hazardous Organic Compound Incinerability." Paper presented at the International Symposium on Incineration of

Hazardous, Municipal and Other Wastes, American Flame Research, Palm Springs, CA, Nov. 2-4, 1987.

Tsang, W. and Shaub, W. "Chemical Processes in the Incineration of Hazardous Materials." In: J. Exner (ed.), Detoxication of Hazardous Waste, Science, Ann Arbor, MI, 1982. p.41.

Tsang, W. Personal Communication. Chemical Kinetics Division, National Bureau of Standards, Gaithersburg, MD., September, 1987.

ACKNOWLEDGEMENTS

Many individuals contributed to this project. Without the invaluable assistance of Mr. Albert F. Oberschlake, the experimental program could not have been carried out. The efforts of Ms. Laurel Staley and Mr. Lou Garcia in assisting with the operation of the turbulent flame reactor (TFR) and collection of the samples is also greatly appreciated. Drs. Barry Dellinger and Wing Tsang supplied data for the low oxygen environment ranking. Mr. Nelson Sorbo, Mr. Richard Steeper and Professor C.K. Law at the University of California, Davis carried out the study of single droplet burning of chlorinated hydrocarbons which made it possible to interpret the results obtained from the TFR. Ms. Shirley Tenhover assisted with the day-to-day functioning of the Thermal Processes Research Group and assisted with the final production of the report on which this manuscript was based. The efforts of Mr. Seldon Heath in the construction of and improvements made to the combustion systems at the Center Hill Laboratory, before this series of experiments began, and whose passing on occurred shortly after his retirement from federal service are also remembered.

This study was made possible with the assistance of a Cooperative Research Agreement #CR-813333-01 which supported one author (Chang) during a sabbatic leave from the University of California, Davis. For that opportunity he is grateful to both the U.S. Environmental Protection Agency and the University of California. The California Air Resources Board supported the effort that was carried out at the University of California, Davis under contract #A6-051-32.

REVIEW OF RESEARCH TESTING ACTIVITIES AT THE U.S. EPA COMBUSTION RESEARCH FACILITY

Robert E. Mournighan
Hazardous Waste Engineering Research Laboratory
U.S. Environmental Protection Agency
Cincinnati, Ohio 45268
and
Larry R. Waterland
Acurex Corporation
Environmental Systems Division
Combustion Research Facility
Jefferson, Arkansas 72079

ABSTRACT

During Fiscal Year 1987(FY87), 25 weeks of incineration testing took place in which 53 individual incineration tests were completed under the operations and research program at the EPA Combustion Research Facility in Jefferson, Arkansas. Test programs completed included: an extended evaluation of the fate of volatile trace metals fed to the liquid injection incineration system (LIS) and testing to evaluate the valence state of chromium discharges from the LIS; testing to support evaluation of the composition of residual discharges from the incineration of five listed hazardous wastes from specific sources; and preliminary evaluation testing of the American Combustion Pyretron Thermal Destruction System as an innovative Superfund site waste treatment technology.

INTRODUCTION

The U.S. Environmental Protection Agency's (EPA) Combustion Research Facility (CRF) in Jefferson, Arkansas, is a 3,100 ft^2 experimental facility which currently houses two pilot-scale incinerators, a rotary kiln incineration system (RKS) and a liquid injection incineration system(LIS), and their associated waste handling, emission control, process control, and safety equipment, with on-site laboratory facilities for waste characterization and analysis of process performance samples.

The objectives of research projects conducted at the CRF have been and continue to be as follows:

- To develop technical information on the performance capability of the hazardous waste incineration process to assist EPA Regional Offices and State environmental agencies in the review, assessment and issuance of reasonable and responsible permits for regulated hazardous waste incineration facilities.

- To develop incinerator system performance data for regulated hazardous wastes to support current incinerator regulations and performance standards, and to provide a sound technical basis for any future standards necessary.
- To develop an understanding of the hazardous waste incineration process that enables the development of methods to predict the performance of incinerators of varying scale and design for the major classes of incinerable hazardous wastes as a function of key process operating variables. These methods would also help to simplify and perhaps reduce the cost of permit and compliance testing.
- To develop methods of improving the reliability and controllability of the incineration process, including the use of destruction and removal efficiency (DRE) surrogates.
- To provide a means of conducting specialized test burns (particularly for high hazard or special waste materials) in support of specific Regional Office permitting or enforcement actions or national priority list site remediation efforts.
- To test the performance of new or advanced incinerator components or sub-systems, or emission control devices.

Three major EPA Program Office regulatory development programs were supported through test activities in FY87 (see Figure 1):

- The hazardous waste incinerator trace metal emission regulation development program within the Office of Solid Waste via testing of the fate of volatile trace metals fed to the liquid injection incineration system (LIS) and testing to evaluate the valence state of chromium discharges from the LIS;
- Evaluating the composition of the residual discharges (scrubber blowdown and kiln ash) from the incineration of listed hazardous wastes from specific sources ("K-wastes"), to support the Agency's Land Disposal Restriction Regulatory Program;
- The Superfund Innovative Technology Evaluation (SITE) program within the Office of Remedial Action and Emergency Response via evaluating the American Combustion (AC) Pyretron Thermal Destruction System as a Superfund site waste treatment technology.

In addition, continuing support of the at-sea incineration program within the Office of Water (OW) was supplied via a 1-week test program (the third such program performed) to continue to validate the marine incineration biological assessment system (MIBAS).

Week ending		Activity	Test days
1986			
October	3	BROS data reduction and report preparation, facility maintenance and repair, and facility decontamination	
	10		
	17		
	24		
	31		
November	7		
	14		
	21		
	26		
December	5		
	12		
	19	Trace metal rangefinding	2 tests
	23		
	31		
1987			
January	9	Trace metal rangefinding	2 tests
	16	Trace metal parametric tests	1 test
	23		1 test
	30		3 tests
February	6		2 tests
	13		3 tests
	20		3 tests
	27		2 tests
March	6	Cr(+3)/Cr(+6) tests	3 tests
	13		
	20	K024 residuals characterization tests	3 tests
	27		
April	3	MIBAS evaluation tests	7 tests
	10	Equipment malfunction (preparing for K001 tests)	
	17	Scrubber and RKS control system repair and upgrade, AC burner system installation	
	24		
May	1		
	8		
	15		
	22		
	29		
June	5		
	12		
	19	AC burner system startup	
	26	Background burn and K001P characterization test	2 tests
July	2	K001 residuals characterization tests	2 tests
	10	AC burner shakedown tests with K001P	1 test
	17		2 tests
	24	K086 residuals characterization tests	1 test
	31	Ram feeder repair	
August	7	K086 residuals characterization tests	3 tests
	14	RKS secondary air installation	
	21	K087 scoping tests	1 test
	28	K087 residuals characterization tests	3 tests
September	4	K037 scoping and BDAT tests	2 tests
	11	K037 residuals characterization tests	1 test
	18	AC burner testing with K087	3 tests
	25		
	30		

Figure 1. CRF test schedule completed: FY87

TRACE ELEMENT EMISSION AND DISCHARGE TESTING

Two series of incineration tests were conducted in FY87 specifically to evaluate the fate of trace RCRA metals fed to the hazardous waste incinerator. The first series of tests was performed in the liquid injection incineration system (LIS) at the CRF. These tests evaluated the fate of arsenic and antimony fed in a synthetic waste mixture and changes in valance state (trivalent/hexavalent) of chromium. Nineteen individual tests (including several "range-finding" tests) were performed over an 11-week period.

In the first series of tests in the LIS the synthetic waste mixture employed mixtures of methanol, chlorobenzene, and carbon tetrachloride, spiked with $SbCl_3$ and As_2O_3. The specific objectives of these tests were:

- To track arsenic and antimony emissions through the incinerator system.
- To study the distribution of metals between flue gas and scrubber blowdown water.
- To explore the relationship between metal emissions and incinerator operating conditions and feed chlorine content.
- To evaluate whether the metals affect waste component destruction.
- To extend the data base on products of incomplete combustion (PIC) emissions from the incineration of chlorinated hydrocarbons.

The test program studied the effects of three variables on the distribution of the trace metals fed among discharge streams: feed chlorine content, incinerator temperature and combustion excess air.

Blends of methanol, carbon tetrachloride and chlorobenzene in the feed produced the various inlet chlorine concentrations (0 to 33.8 percent). Arsenic and antimony compounds were added to these blends in proportions designed to give constant feed concentrations of 12 and 40 ppm, respectively, for all tests.

The liquid feed entered the main combustion chamber of the LIS via a steam-atomized nozzle at about 45 kg/hr (100 lb/hr). Auxiliary propane maintained the incinerator at temperatures that ranged from 1,137° to 1,450°C (2,079° to 2,642°F). Combustion air entered via swirl registers in the burner to result in between 5.9 to 11.7 percent oxygen in the flue gas at the incinerator exit.

EPA reference Method 5 was used to collect samples for particulate loading and arsenic and antimony analyses. The Method 5 train was modified to ensure collection of any antimony and arsenic that passed through the particulate filter of the train. The sample train used consisted of a probe and a glass cyclone, followed by a filter and five impingers. The first impinger contained 0.1 N NaOH. The second, third and fourth impingers contained 0.2 M $(NH_4)_2S_2O_8$ + 0.02 M $AgNO_3$. The last impinger contained silica gel. Following sample collection and digestion, furnace atomic absorption (AA) methods were used to analyze for arsenic and antimony.

During the tests, Method 5 samples were obtained before and after the packed tower (wet scrubber) to determine the effect of scrubbing on the physical state of the compounds (particulate/vapor). Figure 2 shows the results for antimony and Figure 3 shows the arsenic results.

The Figures show that, at the afterburner exit where temperatures were above 760°C (1,400°F), the vapor phase (impinger samples) contained an average of 55 percent of the collected antimony and 35 of the collected arsenic. At the scrubber exit where the temperature was generally at 74°C (165°F), the vapor phase accounted for an average of 6 percent of the collected antimony and 3 percent of the arsenic. Figures 4 and 5 show the effect that chlorine in the feed had on the metal distribution between the vapor and particulate phases in the exhaust gases.

In addition, the data showed that the packed tower had an average collection efficiency of 83 percent for antimony and 92 percent for arsenic.

Chromium Emissions(2)

The liquid injection system was used to determine chromium emissions in the same manner as with arsenic and antimony. Chromium was spiked into the feed for a set of three tests. In the last test, chlorinated compounds (CCl_4 and chlorobenzene) were spiked as well.

Figure 6 shows the collection efficiency of the scrubber system, with and without chlorine. The data show that the chlorine content of the feed may have considerable positive effect on scrubber efficiency.

Figure 7 shows the hexavalent chromium (Cr^{+6}) content of the flue gas particulate and the scrubber water. The values show that between 14 and 17 percent of the chrome measured in each stream consists of the hexavalent species, with the remainder being trivalent chromium.

DESTRUCTION AND REMOVAL EFFICIENCIES (DRE)

The tests demonstrated acceptable DREs for both carbon tetrachloride and chlorobenzene. Chlorobenzene DREs were higher than those for carbon tetrachloride. Carbon tetrachloride DREs were greater than 99.99 percent at the afterburner exit. These increased to greater than 99.999 percent at the scrubber exit. Similarly, chlorobenzene DREs ranged from 99.999 percent at the afterburner exit to generally better than 99.9999 percent at the scrubber exit. The available data do not suggest any discernible effect of temperature, feed composition, excess air, nor the presence of arsenic or antimony on DRE. This is consitent with previous CRF data.

PRODUCTS OF INCOMPLETE COMBUSTION (PICs)

Incineration produces low levels of PICs. The CRF routinely analyzes

FIGURE 2
ANTIMONY

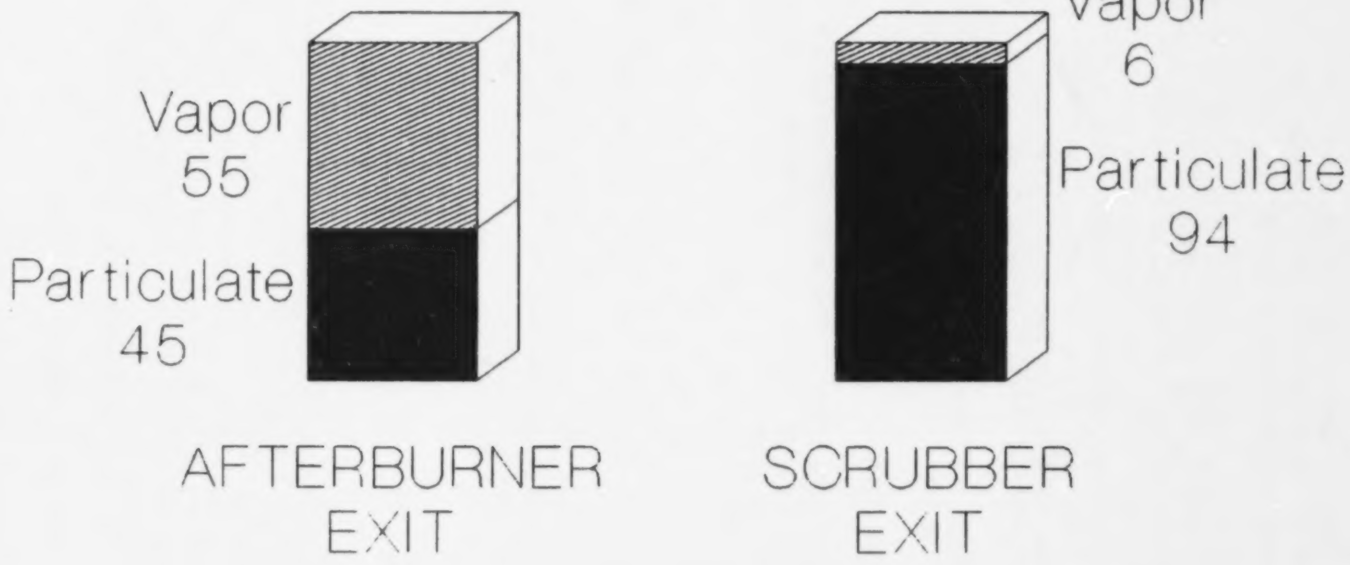


FIGURE 3

ARSENIC

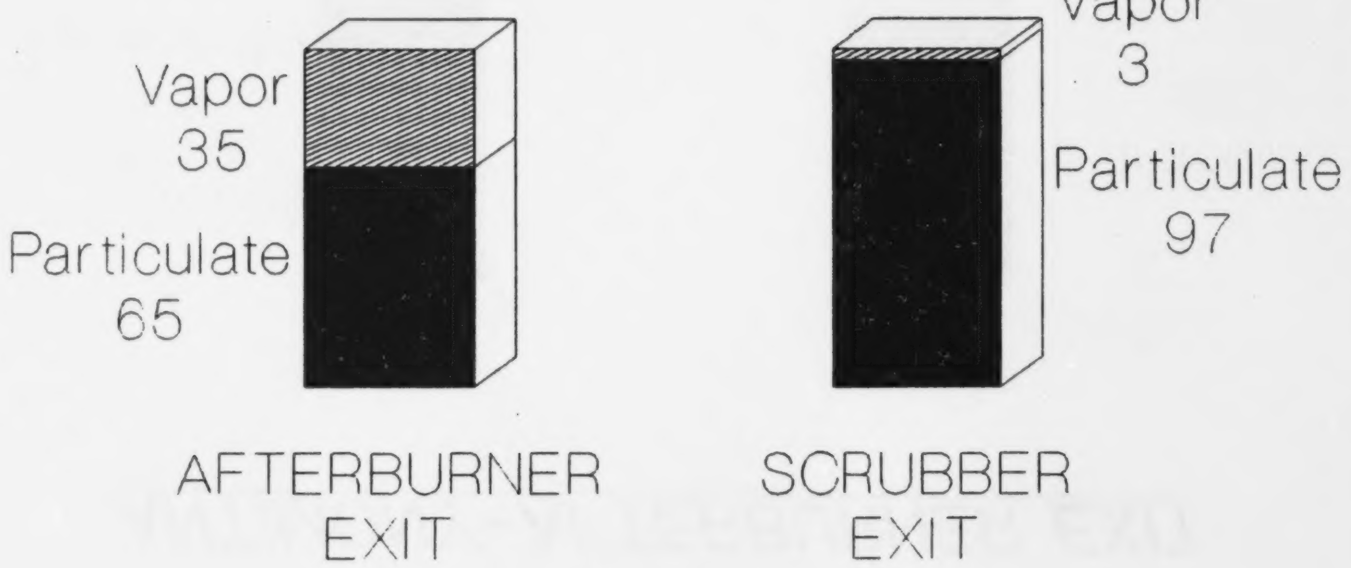


FIGURE 4

ANTIMONY-AFTERBURNER EXIT

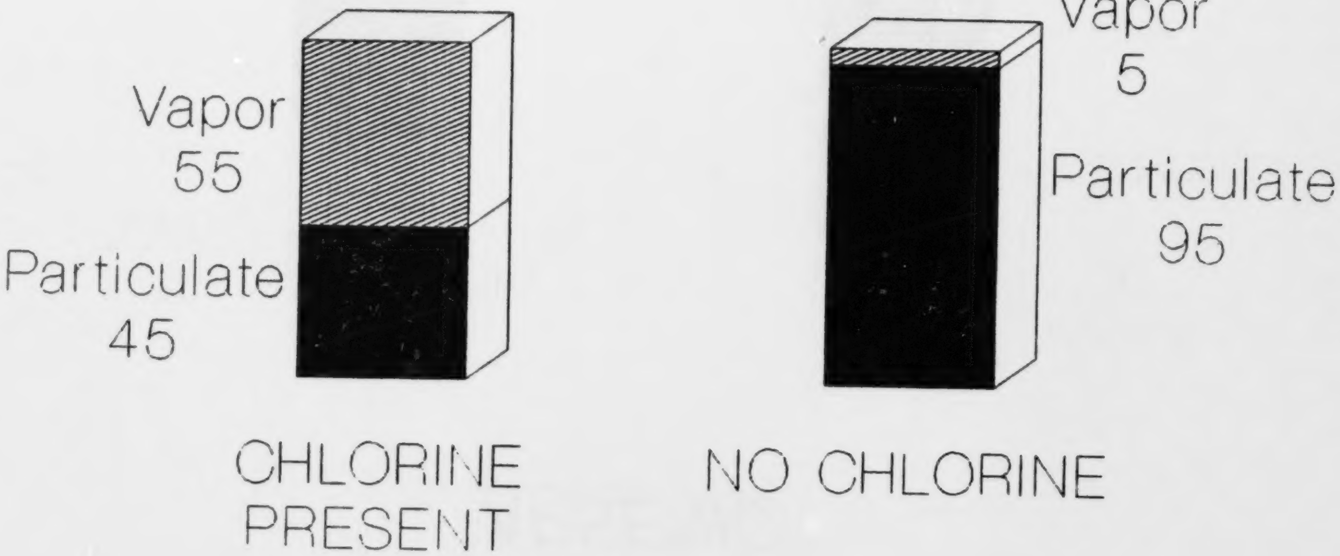


FIGURE 5

ARSENIC AT AFTERBURNER EXIT

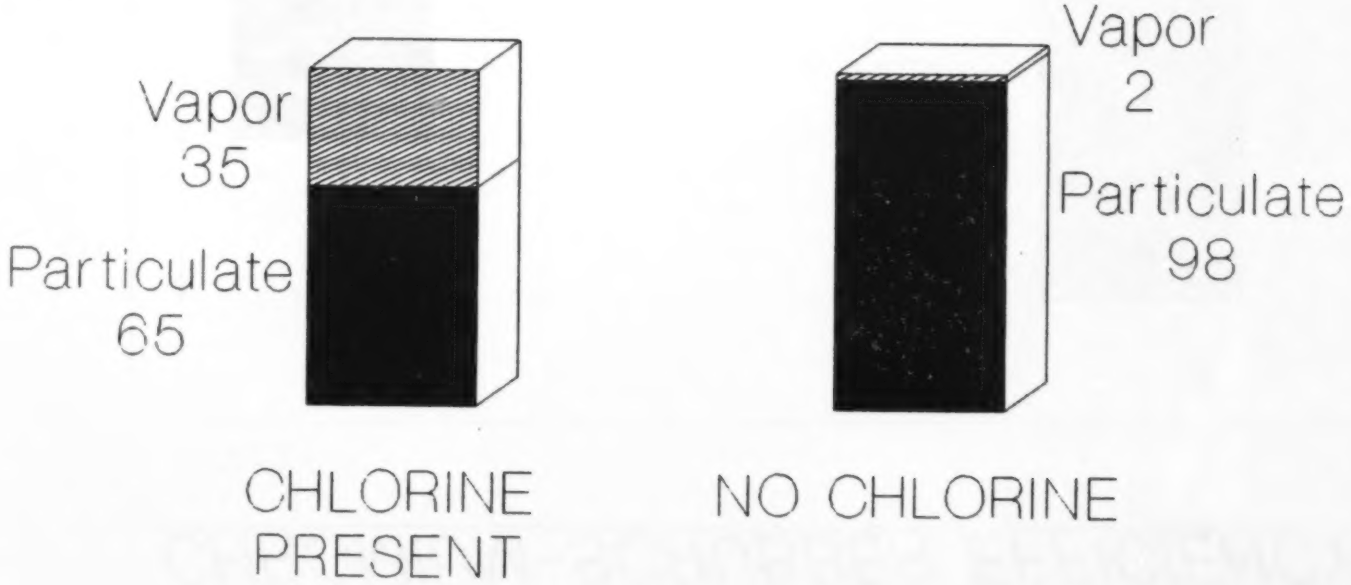


FIGURE 6

CHROMIUM-SCRUBBER EFFICIENCY

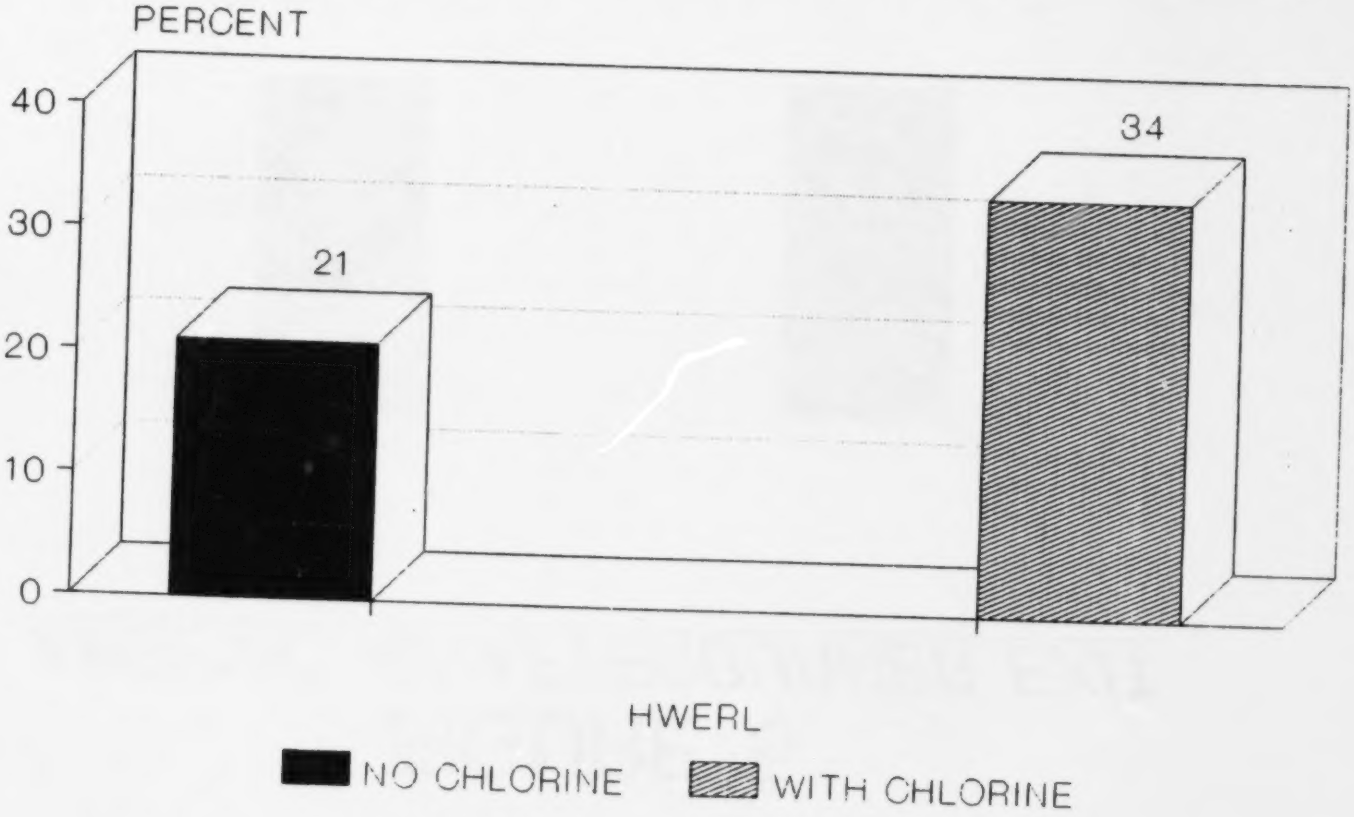
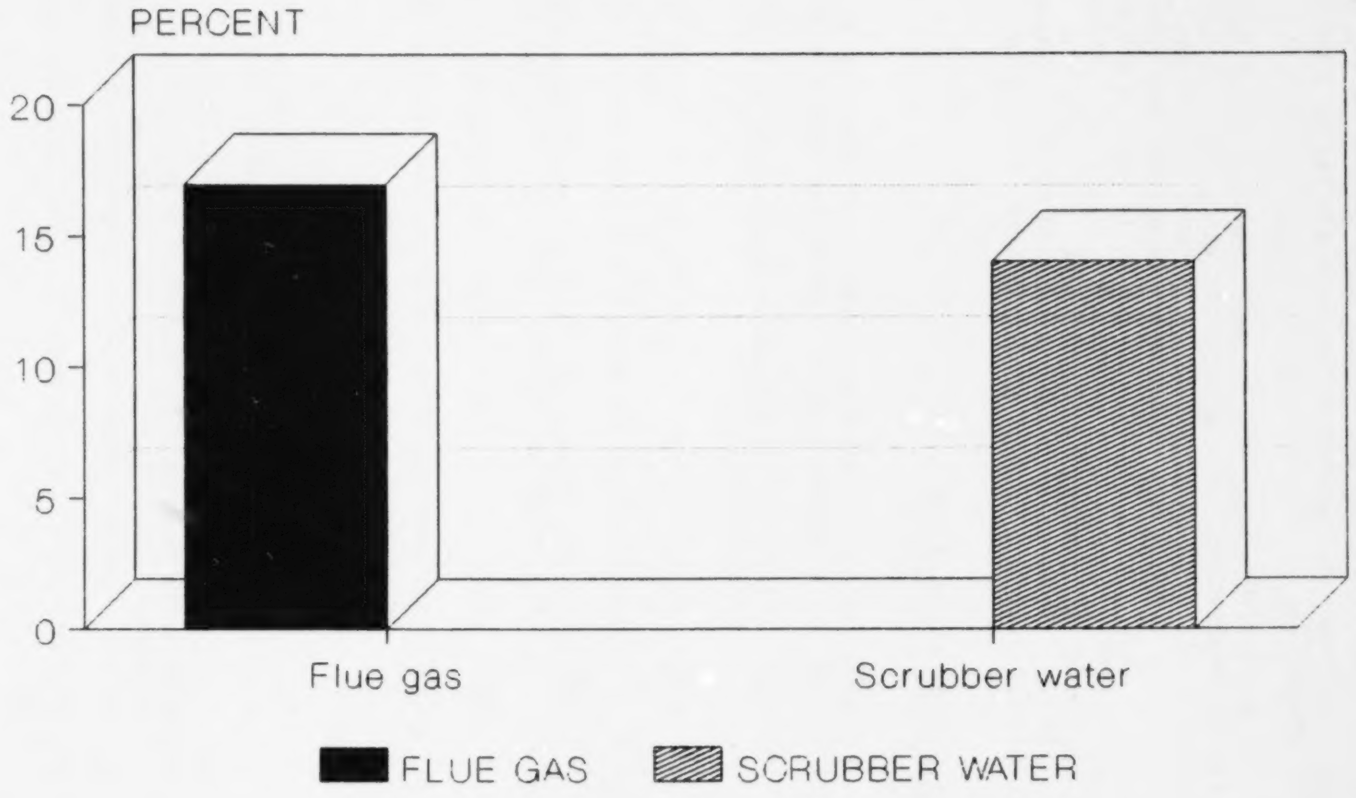


FIGURE 7

HEXAVALENT CHROME



Volatile Organic Sampling Train (VOST) samples for 22 organic compounds with GC/FID. For these tests at the afterburner exit, of these 22 compounds, carbon tetrachloride was present at the highest levels (>100 g/dscm). Other chlorinated alkanes and alkenes were present in the 10 to 100 g/dscm range. Chlorobenzene concentrations were similar to those of the common chlorinated PICs.

At the scrubber exit, PIC concentrations are about one-tenth of those at the scrubber inlet, i.e., afterburner exit. The levels of carbon tetrachloride levels ranged from 4.4 to 31 g/dscm. The highest concentrations occurred at low excess air conditions. Except for one test, chlorobenzene (the other POHC) levels ranged from 1.4 to 14 g/dscm and did not appear to correlate with temperature or excess air. Other PICs include methylene chloride which was present in all tests at relatively high levels (11 to 139 g/dscm). Other chlorinated alkanes and alkenes, hexane, benzene and toluene were present at levels generally below 10 g/dscm.

LISTED WASTE INCINERATION

Incineration testing of five K-wastes was completed at the CRF from late March through early September 1987. The wastes tested were:

- K024: Distillation bottoms from the production of phthalic anhydride from napthalene
- K001: Bottom sediment sludge from the treatment of wastewater from wood preserving processes that use creosote and/or pentachlorophenol (a pentachlorophenol process sludge was tested)
- K086: Solvent washes and sludges from cleaning equipment used in the formation of inks containing chromium and lead
- K087: Decanter tank tar sludge from coking operations
- K037: Wastewater treatment sludges from the production of disulfoton

The specific objectives of the tests were to:

- Establish that these wastes could be incinerated while complying with the hazardous waste incinerator regulations
- Collect representative samples of the incineration residuals along with waste feed samples leading to these residuals and establish the hazardous characteristics (e.g., extraction procedure (EP) toxicity) of the residuals, especially as compared to the parent waste
- Evaluate unit feed systems with actual hazardous wastes with diverse handling properties

Three tests were performed with the K024 waste in late March 1987. Three tests were performed with the K001 waste in late June 1987. One test with a K086 solvent wash waste was performed in late July 1987, and three tests of three different K086 sludge wastes (one test per waste) were performed in early August 1987. One shakedown test and three production tests were performed with the K087 waste in late August. Finally, one shakedown and two production tests were performed with K037 waste in early September 1987. The last tests were the most challenging in that all incinerator operating personnel were required to don Level C protective clothing and equipment. Level B protection for the incinerator room personnel sufficed for the other materials tested.

For all tests except those with the K086 solvent wash waste, waste feed to the kiln was via the drum ram feed system. Thus, for these tests, waste was packaged into 5.7 L (1.5 gal) "pilot-scale" fiberpack drums. These drums were then batch fed, one at a time at a predetermined frequency, into the kiln.

The K086 solvent wash waste was pumped into the kiln via a liquid feed pump/water-cooled feed lance system.

The test period from late June to mid-September 1987 during which four of the five K-waste test programs were conducted, along with two additional test programs discussed in the next section, represented an intensive test period during FY87. Over this period, the facility was in test operation status for 12 weeks out of 14; 21 individual tests were completed.

SITE DEMONSTRATION TESTING

Under EPA's Superfund Innovative Technologies Evaluation (SITE) program, several innovative waste treatment technologies will be evaluated to determine their applicability to Superfund site waste cleanup efforts. Under this program, EPA will fund the evaluation while process vendors will finance the treatment process construction and operation.

A demonstration of the American Combustion, Inc., (ACI) oxygen-enhanced burner system (referred to as the Pyretron Thermal Destruction System) retrofit to the CRF's rotary kiln incinerator system (RKS) is being performed under the SITE program. ACI's proposal to EPA was one selected in the first round of SITE program awards. This demonstration effort is being performed with coordination from the EPA Office of Remedial Action and Emergency Response.

Installation of the Pyretron system into the RKS at the facility occurred during the RKS downtime to effect scrubber system and process control system repairs in the period from mid-April through mid-June 1987. Startup and initial system shakedown efforts were completed in early June. The new burners installed were required to be capable of operating in a conventional mode with air introduction as the only oxidant. Thus, despite the fact that most of the K-waste residuals characterization tests discussed above were performed after installation of the new burner system, these tests were conventional incineration technology with air-only combustion.

After the initial Pyretron system shakedown testing was completed with no waste feed to the kiln (only propane fuel supplied heat input), two series of shakedown, familiarization, and capabilities probing tests were completed. The first of these employed K001 waste feed to the kiln and was completed in early July 1987. Three tests were performed in this initial shakedown series. The first test was performed at the same waste feedrate (50 kg/hr (110 lb/hr) and a drum fed every 3 min) as the K001 residuals characterization tests, but with 35 percent oxygen participation in the combustion process. The second test was performed using a programmed oxygen enhancement response at the same overall waste feedrate, but with the feed mass per charge tripled and the feed frequency at one-third that used in the first test (three 2.5 kg (5.5 lb) drums fed every 9 min). The objective of this test was to establish that the increased transient puffs of uncombusted waste rising out of a batch charge of the waste could be prevented, or their magnitude decreased, via use of the Pyretron system.

The third test, also with programmed oxygen enhancement, was performed at 50 percent increased waste feedrate but the same feed mass per charge as the second test. The overall waste feedrate was increased by increasing the feed frequency (three 2.5 kg (5.5 lb) drums fed every 6 min). The objective of this test was to show that increased waste feedrates could be achieved via use of the Pyretron system.

During this first series of shakedown tests, the opportunity was taken to support another EPA research program, the bioassay protocol evaluation efforts being performed by the Health Effects Research Laboratory (HERL) in Research Triangle Park (J. Lutix, HERL Coordinator, S. Nolan, AEERL Coordinator). In this effort, the CRF provided access for the operation of a dilution tunnel sampling train. The train is designed to collect samples representative of the ambient samples resulting from flue gas discharges from combustion sources.

The sampler was operated during the second two K001 shakedown tests. Plans were to continue to use this sampler during the K086 residuals characterization tests discussed in Section 4; however, scheduling problems prevented this from being realized.

The second series of shakedown/finalization/capabilities probing tests was performed in mid-September using K087 waste. These tests directly followed the K037 waste residuals characterization tests. Two tests were performed. The first test was performed at a waste feedrate of 36 kg/hr (80 lb/hr) with 35 percent oxygen participation in the combustion process. One approximately 1.6 kg (3.5 lb) drum was feed every 2.5 min. The second test was performed with waste feedrate approaching 55 kg/hr (120 lb/hr) with programmed oxygen enhancement. The feed charge mass was doubled to about 1.6 kg (3.5 lb) drums fed per charge. The charge frequency was decreased to approach two drums fed every 3.5 min. The objective of this test was, again, to establish that transient puffs of uncombusted waste arising from each batch charge could be prevented, or their magnitude decreased, and that an increased waste feedrate could be achieved via the use of the Pyretron system. The second test established that 55 kg/hr (120 lb/hr) of this relatively high heating value waste (up to 39 MJ/kg (17,000 Btu/lb)) was just over the maximum waste feedrate achievable in the RKS. Feedrates of this waste at this magnitude result in kiln temperatures near the maximum tolerable.

The full demonstration program planned for this technology will be completed in FY88. The demonstration tests will be conducted using waste material excavated from the Stringfellow Superfund site near Riverside, California, mixed with K087 waste. The objective of the demonstration tests is to provide the data to evaluate three ACI claims regarding the Pyretron system as follows:

- The Pyretron system with dynamic oxygen enhancement reduces the magnitude of the transient high levels of organic emissions, CO, and soot ("puffs") that occur with repeated batch charging of waste fed to a rotary kiln
- The Pyretron system with oxygen enhancement is capable of achieving the RCRA mandated 99.99 percent destruction and removal efficiency (DRE) of principal organic hazardous constituents (POHCs) in wastes incinerated at a higher waste feedrate than conventional, air-only, incineration
- The Pyretron system is more economical than conventional incineration

REFERENCES

1. Lee, J.W., Ross, R.W., Vocque, R.H., Lewis, J. and Waterland, "Distribution of Trace Element Emissions from the Liquid Injection Incinerator System Combustion Research Facility," EPA/600/S2-87/054 Sept. 1987.

2. Draft Report: Lee, J.W. et al. "Distribution of Total and Hexavalent Chromium in Emissions and Residuals from Pilot-Scale Liquid Injection Incineration," March 1988.

PILOT-SCALE BOILER COFIRING TESTS TO INVESTIGATE NONSTEADY EFFECTS

H. B. Mason, J. A. Nicholson, R. J. DeRosier, and C. D. Wolbach
Acurex Corporation
Mountain View, California 94039

and

I. J. Licis
U.S. Environmental Protection Agency
Cincinnati, Ohio 45268

A simulated waste of semivolatile and volatile chlorinated organics was cofired with gas, oil, and coal in a 2 million Btu/hr boiler simulator operated under transient and off-design conditions. Nonsteady and off-design operating modes tested include low excess air firing, atomization upsets, transient firebox temperatures, and variable firing rate, residence time, and waste of fuel flowrates. Waste destruction results showed uniformly high destruction efficiencies (DE) even under major upset conditions where combustion conditions were poor. The test average DE was 99.9993 percent for volatile compounds and 99.9997 for semivolatiles compared to the average of 99.998 percent for various field tests. Waste destruction was generally less efficient under upset conditions compared to normal operation. Products of incomplete combustion (PICs) were emitted at average levels about seven times the emissions of principal organic hazardous constituents (POHCs). The analytical procedures accounted for about 90 percent of chlorinated volatile PICs and about 80 percent of nonchlorinated hydrocarbons. Residual emissions of POHCs and PICs were observed after waste firing was curtailed. The hysteresis emission levels immediately after waste firing were of the same order as emissions during normal operation; they were generally lower than emissions during upsets. The severity of the hysteresis generally increased as the boiler heat transfer surfaces became increasingly loaded with soot and ash deposits. Emissions were higher than normal when deposits were being removed by sootblowing. The severity of hysteresis was reduced after sootblowing.

INTRODUCTION

The basis for the impending EPA boiler cofiring regulations is largely the test data from a series of 14 industrial boiler cofiring field tests conducted by EPA from 1982 to 1986. These tests were run to determine the capabilities of industrial boilers for waste destruction under both well-controlled and routine operation. The boiler test facility specifications and operating conditions were selected to obtain a reasonable coverage of the diverse range of industrial boiler designs and operating practices. Field test data were obtained for the following range of conditions:

- Firetube, package and field-erected watertube designs; 0.3 to greater than 2 seconds residence time in main firebox
- 2,500 to 350,000 lb/hr steam capacity
- Gas, oil, coal, and wood fuels
- Volatile and semivolatile wastes with a heating value from 0 to 18,000 Btu/lb
- 0 to 100 percent heat input from wastes

The results of these 14 tests showed an overall mass-weighted waste destruction efficiency of 99.998 percent. This high level of destruction was generally exhibted across the broad range of designs, waste characteristics, and operating conditions tested and prevailed even when the boilers were intentionally operated in off-design upset conditions such as substoichiometric air, malfunctioning atomizers, and waste flow transients. In fact, the destruction efficiencies were so uniformly high that it was not generally possible within the constraints of plant operation to identify and run test conditions where the destruction was not acceptable.

Although the field test data base supporting the proposed standard indicates uniformly high destruction efficiencies, additional information and analysis is needed to interpret several patterns observed in the data and to generalize the effects of operation on destruction efficiency. One pattern observed in the field tests was variability in DE results of up to an order of magnitude, which was apparently not due to artifacts in the sampling and analysis scheme or to contamination. Additionally, the variations did not correlate with any boiler operational settings or with boiler performance indicators such as CO or NO_x emissions or smoke. It was also observed at several sites that the stack concentrations of waste species continued for several hours after waste firing was curtailed. This hysteresis effect may be attributable to deposition of trace concentrations of waste species on boiler surfaces, particularly on areas with carbonaceous deposits from oil or coal firing. A potential role of soot deposits in the observed hysteresis and stack emission variability was also indicated by limited sootblowing results that showed higher emissions during routine sootblowing from the boiler convective section than during normal operation. To gain more confidence in the field test data and assist in the data interpretation, data are needed to isolate the presence and extent of emission variability and to relate these data to operational settings and the conditions of the boiler heat exchange surfaces.

A second key issue from the field tests is a more comprehensive characterization of the types and quantities of PICs emanating from the POHCs, or from the conventional fuel. Several tests showed PIC emissions in boilers as a higher fraction of the organic compounds in the flue gas than were observed in incinerators. More data are also needed on the effects of operating conditions on the relative concentrations of PICs and POHCs.

A third issue is the degree to which nonsteady or off-design boiler operation affects destruction efficiency. The field tests were somewhat limited in the types and severity of imposed upsets but showed a broad operational window with high destruction efficiency. To generalize this observation, more data are needed on the effects on destruction of various types of upset imposed with more severity than was possible in the field.

An additional issue, not reported on in this paper, is the form and fate of heavy metals contained in the waste or fuel.

The present pilot-scale tests addressed the above issues. The pilot-scale approach was selected because of wider operational flexibility, tighter experimental control, and lower cost compared to field testing.

TEST PROGRAM

To address the issues cited above, seven test series were run, as follows:

I	Baseline -- fuel only
II	Baseline -- cofiring
III	Data variability, replication, and destruction
IV	Evaluation of operational window for high destruction
V	Form and fate of trace metals
VI	Evaluation of PIC production
VII	Confirmatory tests

The series I and II baseline tests were run to obtain reference levels of waste and PIC emissions under weel-controlled operation and for clean heat exchange surfaces in the facility. These results were used for reference-level comparison to later runs in series III and IV as deposits continued to build on heat exchange surfaces, thereby indicating the relative magnitude of background levels or organics and the transient, hysteresis, buildup of the background. Series III was intended to gauge the confidence level in the destruction data relative to variability and reproducibility effects. With this level established, the remainder of the test plan was directed at determining the effect of operating conditions on POHC, PIC, and metal emissions.

Series IV provided for parametric testing of various off-design and upset operating conditions to attempt to define the operating boundary of the high DE window. Operating parameters tested included low excess air; atomizer upsets; heat exchange designs affecting residence time and firebox temperature; firing capacity; and waste or fuel flow transients. Series V focused on doping the flame with metal species of interest in the regulatory proces: arsenic, cadmium, chromium, and lead, and sampling for metal concentrations in several size fractions. Series VI featured a spot check of substituting inorganic chloride for the chlorinated waste to determine if waste identity influences PIC identity over and above the presence of chlorine. The final runs in series VII were designed to test conditions which, on the basis or prior results, showed potential for confirmation of DE levels and trends.

TEST FACILITY

The pilot-scale facility used for these test series is a refractory-lined furnace and convective section designed with geometric similarity and time-temperature simulation of a tangentially or wall-fired watertube boiler, as shown in Figure 1. For the present tests, the unit was fired in the wall-fired mode, typically with gas, oil, or coal fired through three of the burners and a simulated waste through the remaining burner. The fuel feed system, cooling system, and post-combustion cleanup system are shown schematically in Figure 2. For most tests, the unit was fired at a rate of 1.5 million Btu/hr, which gives a residence time and temperature history in the firebox representative of full-scale boilers in the radiative and early convective sections, as shown in Figure 3.

The wall-fired burners were variable-swirl research burners equipped with a single fuel injector tube. Combustion air was preheated to upstream of the burner by an electric heater. Steam atomization was used for oil and waste firing. The convective section consists of approximately 20 tube bundle heat exchange drawers that are cooled to about 300°F with Dowtherm.

For oil firing, a 2.2 percent sulfur residual oil with a heating value of 18,300 Btu/lb was used for the three burners fired on conventional fuel. The oil was heated to about 220°F by drum heaters and heat traced recirculation loops. For coal firing, an Illinois No. 6 coal with a 3.6 percent sulfur content was pneumatically conveyed to the burners.

The synthetic waste fired through the remaining burner was a blended mixture of 80 percent by weight No. 2 distillate oil and 5 percent each carbon tetrachloride, trichloroethylene, monochlorobenzene, and trichlorobenzene. The mixture was recirculated continually with a pump to retard stratification and fed to the steam-atomized burner at room temperature. For baseline testing in the absence of waste, all four burners were fired on conventional fuel.

Thermocouples, sampling ports, and viewports were positioned along the furnace and convective section. Temperatures, flowrates, and emission measurements were recorded and processed on a microcomputer or datalogger. Continuous monitoring was done for O_2, CO (two scales), CO_2, hydrocarbons, SO_2, and opacity.

Volatile waste constituents and PICs were sampled in the flue gas with the VOST. Two methods of using the VOST were employed. For periodic comprehensive quantification, the full-VOST sampling protocol was used with gas chromatography/mass spectroscopy (GC/MS) analysis following thermal desorption. To reduce the cost and turnaround time for multiple samples, a reduced protocol, termed "mini-VOST," was used. The sampling was done on a single VOST trap for 10 minutes, and then the trap was taken to a nearby gas chromatograph and desorbed to a parallel flame ionization detector and a Hall detector to quantitate hydrocarbons and chlorinated species, respectively. This procedure can provide near-real-time feedback on volatile organic waste concentrations.

Semivolatile wastes and PICs were sampled by a Modified Method 5 train fitted with an organics module containing 65 grams of XAD resin. The train was typically run for approximately 4 hours to a total sample volume of 4.3 dscm (150 dscf). The expended XAD was Soxhlet extracted, along with other catches from the Method 5, and analyzed with the GC/MS.

RESULTS

To address the test objectives, 30 test series were run over 28 test days during early 1987. The resultant sampling and analysis for these runs included 151 full-VOST or mini-VOST runs for volatile organic speciation and 18 Modified Method 5 runs for semivolatile organic speciation. Samples were taken for normal routine operation, as well as for a range of induced upset conditions, and during sootblowing. For several runs, samples were taken at up to four stations ranging from the near flame region out to the flue gas. Simultaneous mini-VOST and Modified Method 5 sampling was done at two stations to detect differences due to residence time or temperature during upset runs. Samples were also taken at specified intervals after waste firing was stopped to detect the amount and duration of any hysteresis emission "tail."

Tables 1 and 2 summarize the overall test average DE for volatile and semivolatile POHCs, respectivley. The tables also include a total POHC plus PIC result. For these tables, PICs were specified as volatile or semivolatile chlorinated organics. This designation was based on the fact that the POHCs were all chlorinated. Some chlorine was also contained in the parent fuels however, and that could yield some nonwaste-related PICs. Also, the chlorinated POHCs could produce nonchlorinated PICs. These factors preclude a precise identification or closure of PICs.

The overall mass-weighted DE average was 99.9993 percent for the three volatile POHCs and 99.9997 percent for the semivolatile POHC. These destruction efficiencies are higher than the 99.998 percent average for the field tests, possible because the pilot-scale system was intentionally clean of POHC deposition at the outset of the testing. The differences cited in DE among the three fuels and the volatile POHCs were not major; and, in all cases, DE was well above 99.99 percent, even when total chlorinated POHC plus PIC compounds were included as an aggregate.

The DE results on Figures 4 and 5 do not show a strong effect in going from normal operation to upset operation. This observation requires some interpretation in relation to what constitutes an upset. In this regard, Figures 4 and 5 show DE as a function of average flue gas CO emissions (corrected to 7 percent oxygen) during a run. Figure 4 shows total chlorinated volatile compounds, POHCs plus PICs, and Figure 5 shows only the carbon tetrachloride results. These results show some correspondence between higher destruction at low CO and fewer high destruction results at high CO. These plots are useful to discuss the concept of upset operation. Some of the very low CO results shown in Figures 4 and 5 were operationally classified as upsets since they involved atomization maladjustments, waste flow surges, and other off-spec or tranisent settings. In some cases, these settings did not result in CO or other emission excursions and would not be classified as upsets if an emission-based criteria were used to segregate "normal" operation from "upset" operation.

Figures 6 and 7 show the normal and upset results when the upset designation is arbitrarily assigned to any run with an average CO level above 200 ppm. This procedure thereby reclassifies as normal the runs initially designated as upsets but with low CO. This approach to segregating runs by CO emissions shows a generally significant and consistent trend of lowered destruction efficiency resulting from upsets producing combustible emissions. This result for the pilot-scale tests is more pronounced and consistent than was observed in the field tests, possibly because of higher background emissions and hysteresis effects with the field boilers. In Figure 7, "C", "G", and "O" refer to coal, gas, and oil, respectively, and "U" and "N" refer to upset and normal. The only situation that deviated from the trend cited above was for monochlorobenzene cofired with coal. All other combinations showed lower destruction efficiency under upset conditions.

One of the purposes of the present tests was to examine the nature and extent of background emission variability or noise and hysteresis. The facility was initially free of POHC exposure and waste firing was introduced only after fuel baselines. The results showed that during the fuel baseline and the early days of cofiring, the POHC and PIC emission levels were very low, frequently nondetectable. As the upset operating settings were introduced and the deposits built up on the convective section, background emissions began routinely appearing. These background emissions were quantified by sampling after cofiring was stopped, with the unit operating on gas only. The level of the background appears to depend on the elapsed time since cofiring had been curtailed, on the types of upsets imposed prior to stopping cofiring, and on the total number of days of facility exposure to

POHCs. The background, or hysteresis, thus appears to have both short-term and long-term components.

Figure 8 shows the residual emissions at various intervals after cofiring was curtailed for total volatile chlorinated POHCs and PICs. There is a general trend for the background to decay with elapsed time since cofiring. At the 15- and 65-hour samples, there are numerous data points on the abcissa that outweigh the outliers. It should be emphasized that this facility was operated on waste for 6 to 8 hours per day, 5 days per week, and on gas only during the remaining time. The deposits, therefore, had an opportunity to bake-out or desorb during nights and weekends. Alternate duty cycles could cause the hysteresis results to differ.

Figure 9 shows the historical variation of the hysteresis effect by comparing emissions sampled at 15 hours after cofiring cessation, but at different total number of days' operation of the facility on waste. These results show a general tendency for the background emission levels to increase with exposure of the facility to POHCs. Soot was blown from the tubes on day 50, which may account for the higher backgrounds around day 40.

Emissions were measured during sootblowing at 5 separate stations of the convective section. Results indicate that significant organics were emitted during sootblowing from the first three high-temperature stations. Emissions during sootblowing were up to an order of magnitude higher than normal. Subsequent tests showed lower emissions after sootblowing than during normal operation. Hysteresis results also were lower after sootblowing than during operation with deposits on tubes.

The identification and quantification of PICs generally showed a reasonable level of closure. Mini-VOST chromatograms were run for the flame ionization detector, which shows primarily nonchlorinated hydrocarbons and the Hall detector, which speciates chlorinated organics. The PICs identified were similar to the compounds identified in the field tests from the full-VOST analysis. The total emission loading quantified for chlorinated organics was generally over 90 percent of the total chromatogram response. The closure on PIC identification for hydrocarbons was about 80 percent of the emission loading basis. The closure on the number of peaks identified was lower because of the large number of hydrocarbon species emitted in small quantities. For the semivolatile chromatogram, most of the large peaks were identified, but due to a strong background emission level, the closure on total emissions was only about 50 percent.

The mass-weighted ratios of PICs to POHCs in the flue gas are listed in Table 3 for volatile and semivolatile chlorinated compounds. The mass-weighted average for volatile compounds was about 7, somewhat lower than the average of about 15 observed in the field. Table 3 and Figure 10 also show a pseudo PIC-based DE which compares volatile chlorinated PIC emissions to POHC feedrate to the boiler. The PIC with increasing CO trends are similar to the decreasing destruction efficiency observed for POHCs.

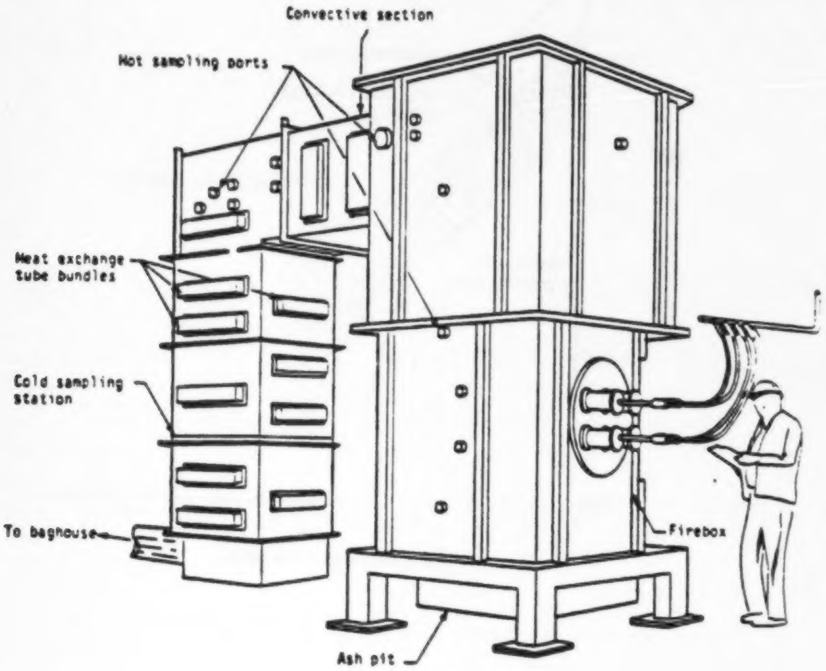

Convective section
Hot sampling ports
Heat exchange tube bundles
Cold sampling station
To baghouse
Firebox
Ash pit

Figure 1. Pilot-scale experimental furnace

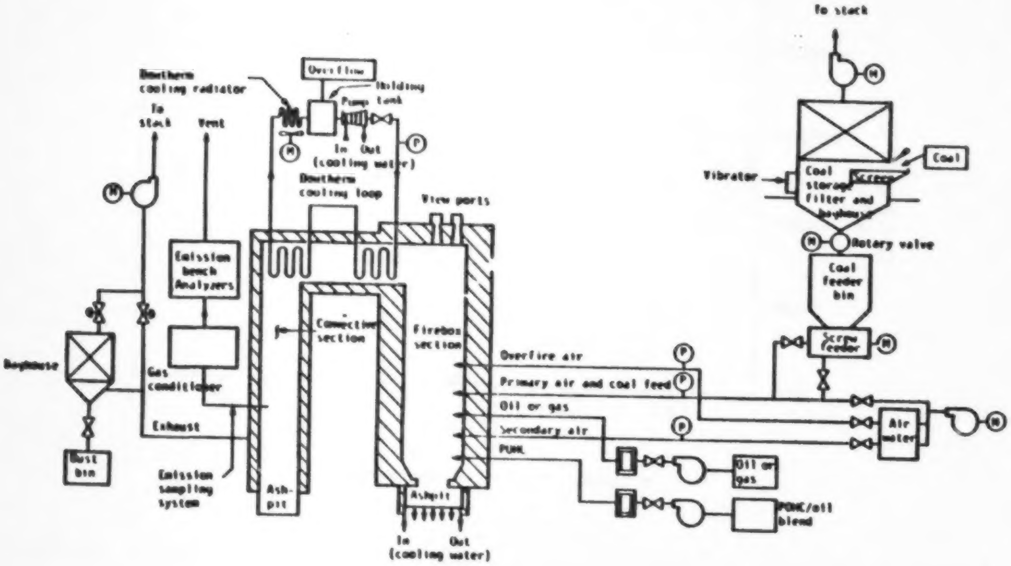

To stack
Dowtherm cooling radiator
Overflow
Holding tank
Pump
To stack
Vent
M
In Out (cooling water)
P
Dowtherm cooling loop
View ports
M
Emission bench Analyzers
Baghouse
Gas conditioner
Exhaust
Dust bin
Emission sampling system
Convective section
Firebox section
Ash-pit
Ashpit
In Out (cooling water)
Vibrator
Coal storage filter and baghouse
Screw
Coal
M
Rotary valve
Coal feeder bin
Screw feeder
M
Overfire air
Primary air and coal feed
Oil or gas
Secondary air
PUHL
P
Air meter
M
Oil or gas
PUHC/oil blend

Figure 2. Pilot-scale research furnace system

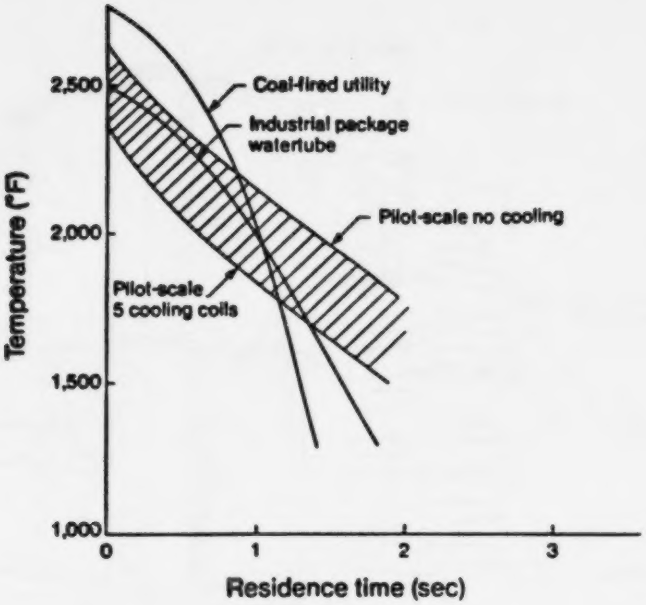


Figure 3. Time-temperature simulation

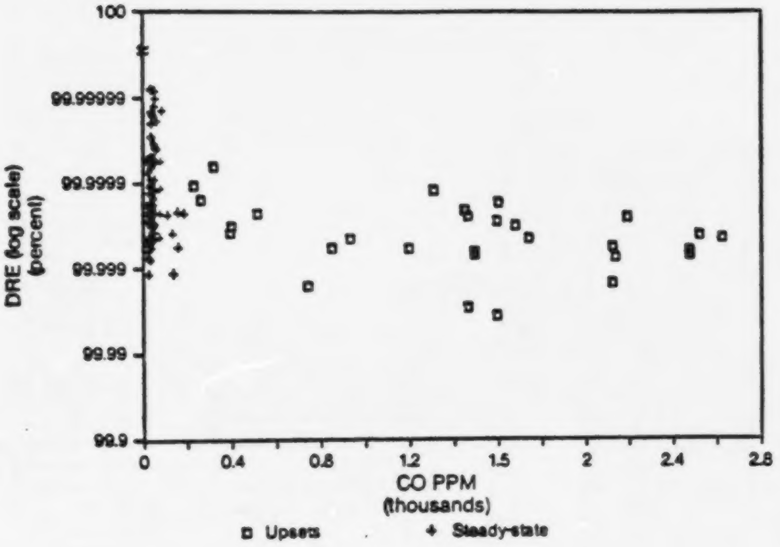


Figure 4. Effect of upsets on DRE: total volatile chlorinated species

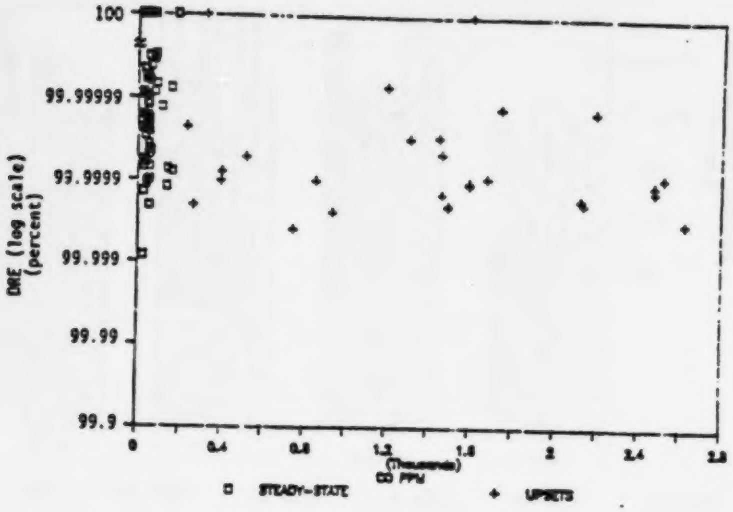


Figure 5. Effect of upset on DRE: CCl_4

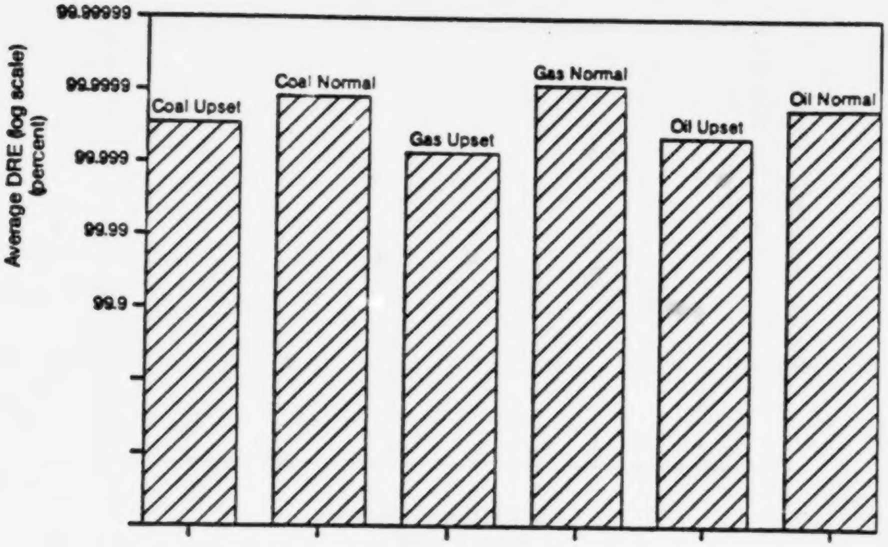


Figure 6. Effect of upsets: total volatile chlorinated species

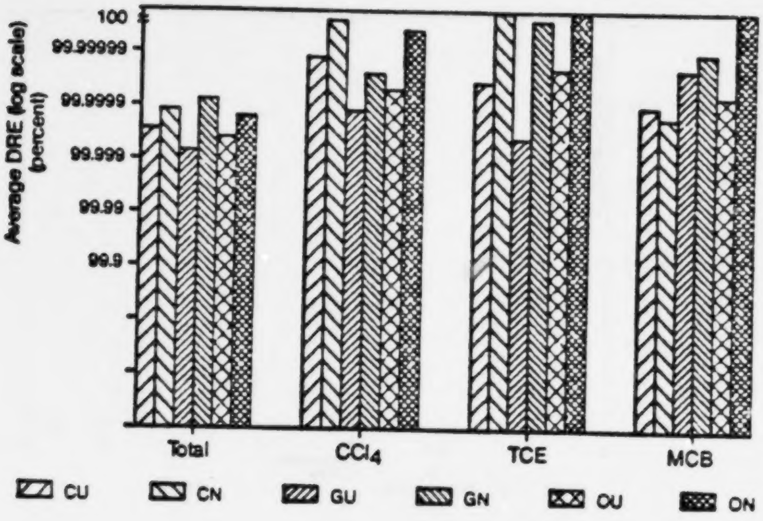


Figure 7. Effect of upsets: POHC and fuel effect

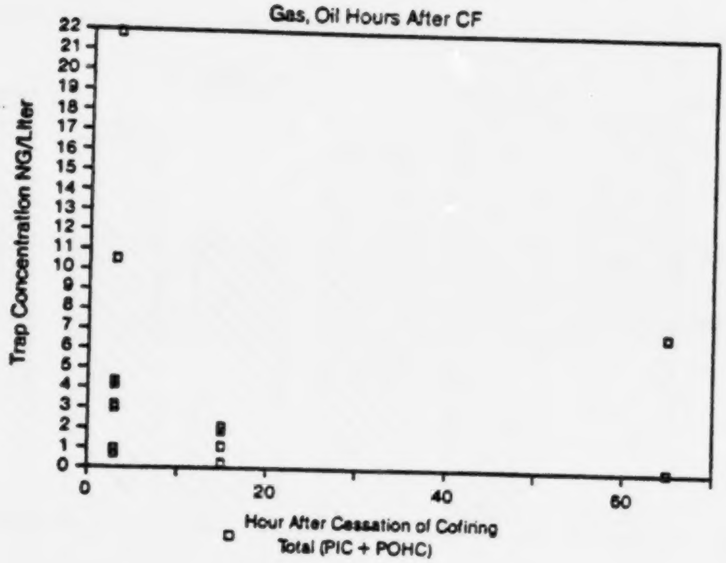


Figure 8. Hysteresis: total volatile organic species measured after cofiring

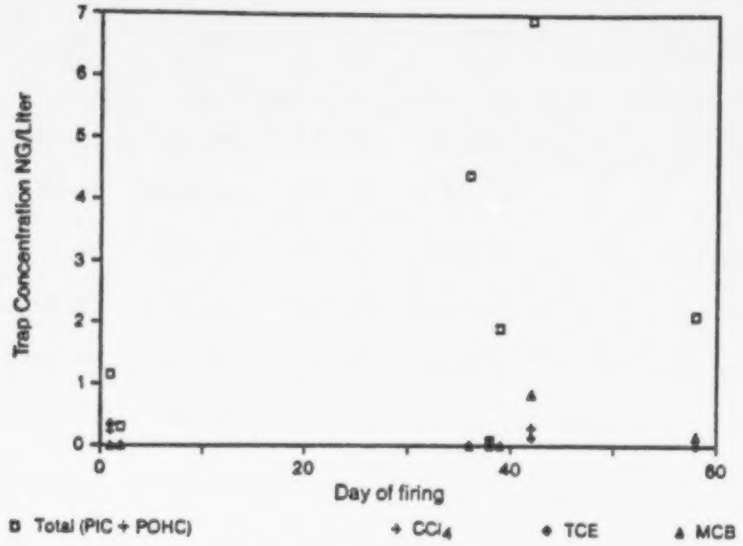


Figure 9. Hysteresis: samples taken 15 hours after cofiring

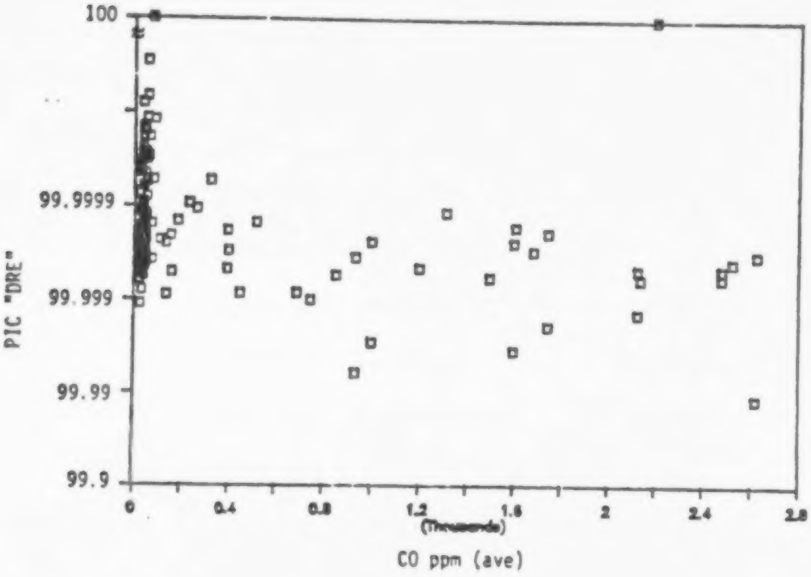


Figure 10. PIC-CO correlation

TABLE 1. VOLATILE DRE SUMMARY

	POHC + PIC	CCl_{14}	TCE	MCB
Gas	99.9952	99.9991	99.9977	99.9994
Oil	99.9960	99.9997	99.9995	99.9995
Coal	99.9963	99.9998	99.9993	99.9973
Normal	99.9995	99.9997	99.9998	99.9996
Upset	99.9982	99.9995	99.9981	99.9983
Overall average	99.9961	99.9997	99.9993	99.9992

TABLE 2. SEMIVOLATILE DRE SUMMARY

	POHC + PIC	TCB
Gas	99.99945	99.99994
Oil	99.9988	99.99993
Coal	99.99921	99.99917
Normal	99.99938	99.9998
Upset	99.99928	99.99976
Overall average	99.9993	99.99978

TABLE 3. PRODUCTS OF INCOMPLETE COMBUSTION

	Volatile DRE	PIC/POHC	Semivolatile DRE	PIC/POHC
Gas	99.99906	4.1	99.99953	9.8
Oil	99.99967	11.5	99.99941	2.8
Coal	99.99912	3.2	99.99921	1.0
Normal	99.99977	7.8	99.99973	4.0
Upset	99.99895	11.2	99.99933	2.1
Overall average	99.99953	7.2	99.99945	2.6

OXIDATION OF POLYCHLORINATED BIPHENYLS BY *PSEUDOMONAS PUTIDA* LB400

by: Sadhana Singh, Frank K. Higson, Louise M. Nadim and David T. Gibson,
Center for Applied Microbiology
The University of Texas at Austin
Austin, Texas 78712

ABSTRACT

Pseudomonas putida LB400 was originally isolated from an environment contaminated with polychlorinated biphenyls. Gas chromatography/mass spectrometry analyses revealed that this organism has the ability to degrade a wide range of individual chlorinated biphenyls. However, little information is available on the initial reactions involved in the degradation of these compounds. Biphenyl-grown cells were shown to oxidize 2,2'-, 2,5,2'5'-, 2,4,5,2',5'-, and 2,4,4'-chlorobiphenyls and some reaction products were tentatively identified by gas chromatography/mass spectrometry. Under the same experimental conditions 4,4'- and 2,4,3',4'-chlorobiphenyls were not metabolized. Similar results were obtained with an enzyme preparation from biphenyl-grown cells of *P. putida* LB400. Current studies are directed towards identifying the reaction products formed from the above chlorinated biphenyls by intact cells and purified enzymes.

INTRODUCTION

Polychlorinated biphenyls (PCBs) are extremely stable compounds and have been used extensively by industry in capacitors, transformers, dielectric fluids, fire retardants and plasticizers (8,10). Although these compounds (Aroclors) are no longer synthesized for use in open systems considerable amounts of PCBs have been introduced into the environment where they tend to persist for long periods of time.

The resistance of highly chlorinated PCBs to biodegradation by aerobic organisms has been well documented (5,6) and their lipophilic properties have led to their concentration in organisms at the end of food chains. Nevertheless, evidence has been presented to show that PCBs, particularly the more highly chlorinated isomers and congeners, can undergo microbial reductive dehalogenation in anoxic sediments (4). Since many of the lower (less heavily chlorinated) PCBs are known to be susceptible to degradation by aerobic bacteria it is not inconceivable that protocols could be developed for the removal of PCBs from certain polluted environments.

In the present study we have focused on the ability of biphenyl-grown cells of *P. putida* LB400 to degrade 2,2'-, 4,4'-, 2,4,4'-, 2,4,3',4'-, 2,5,2',5'-, and 2,4,5,2',5'-chlorobiphenyls (CBs). This organism is thought to metabolize biphenyl by the reactions shown in Figure 1 (9) and it was anticipated that chlorinated analogs of these metabolites would be produced during the degradation of the individual PCBs.

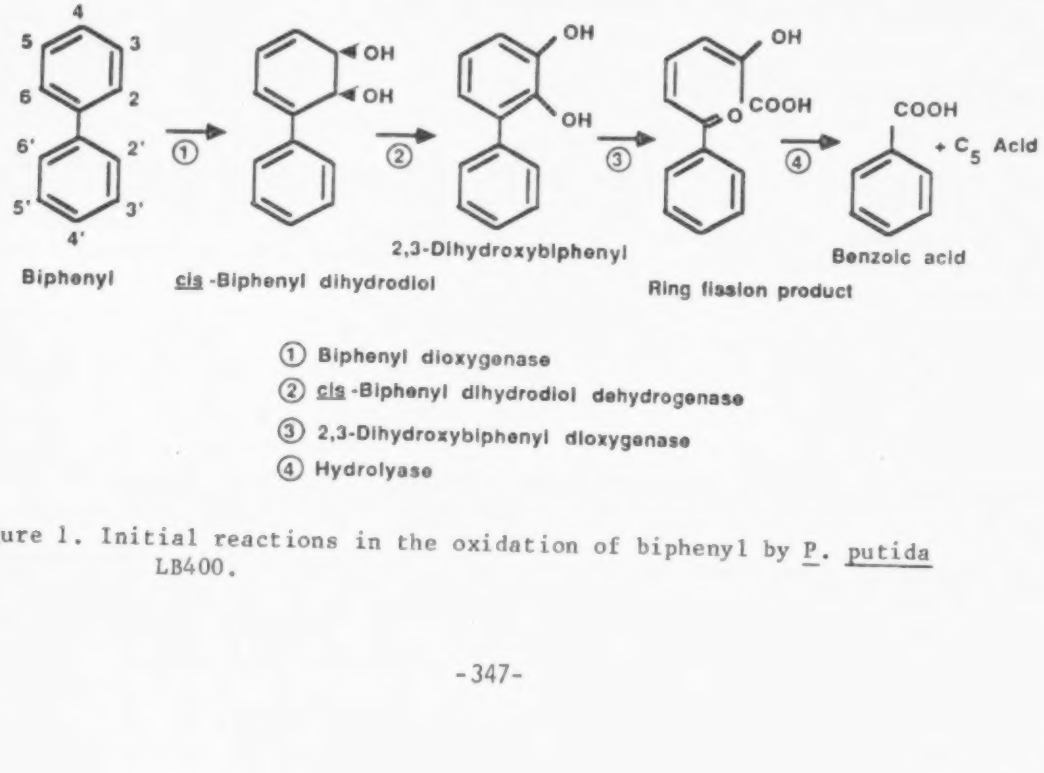

4
5
3
6
2
6'
2'
5'
3'
4'
Biphenyl
①
OH
OH
cis-Biphenyl dihydrodiol
②
OH
OH
2,3-Dihydroxybiphenyl
③
OH
O
COOH
Ring fission product
④
COOH
+ C5 Acid
Benzoic acid
① Biphenyl dioxygenase
② cis-Biphenyl dihydrodiol dehydrogenase
③ 2,3-Dihydroxybiphenyl dioxygenase
④ Hydrolyase

Figure 1. Initial reactions in the oxidation of biphenyl by *P. putida* LB400.

MATERIALS AND METHODS

MICROORGANISMS AND GROWTH CONDITIONS

Pseudomonas putida strain LB400 was originally isolated from a PCB-contaminated site by enrichment culture with biphenyl as the sole source of carbon and energy (3). The organism was grown in 50 ml of mineral salts medium containing sodium succinate (0.2% w/v) as the source of carbon. After growth at 30° C for 9 hours biphenyl (0.1% w/v) was added to the culture medium and growth allowed to continue for a further 9 hours. At this time the cell suspension was filtered through glass wool to remove residue biphenyl and centrifuged at 10,000 x g for 15 min. The cells were washed twice with 0.05M KH_2PO_4 buffer pH 7.5 and resuspended in 50 ml of the same buffer.

TRANSFORMATION EXPERIMENTS

Transformations of individual PCBs were carried out in 250 ml conical flasks containing 50 ml of biphenyl-induced cells at a turbidity of 1.0 at 600 nm. Substrates (0.5 mg in 0.05 ml of methanol) were added to each flask. At designated times the contents of each flask were extracted three times with ethylacetate. The organic phase was dried over anhydrous sodium sulfate and the solvent removed *in vacuo* at 30° C. The residue remaining in the flask was dissolved in 1.5 ml of methanol and stored in 3.0 ml vials until required for analysis by high pressure liquid chromatography (HPLC) or gas chromatography/mass spectrometry (GC/MS).

PREPARATION OF CELL EXTRACTS

Biphenyl-grown cells of *P. putida* LB400 were disrupted by sonication and centrifuged at 100,000 x g for one hour. The clear supernatant solution was used as a source of crude cell extract. The ability of cell extracts to oxidize biphenyl and PCBs was determined polarographically using a Clarke-type oxygen electrode.

RESULTS

OXIDATION OF SELECTED PCBs BY BIPHENYL-INDUCED CELLS OF *P. PUTIDA* LB400.

Table 1 shows that there is considerable variation in the rates of degradation of certain PCBs. The rates observed appear to be a function of the position, rather than the number, of chlorine substituents. Thus 2,2'-CB is rapidly metabolized whereas in the same time period 4,4'-CB was not attacked. In contrast to 4,4'-CB and 2,4,3',4'-CB, the trichlorinated 2,4,4'-congener was significantly metabolized during the one hour incubation period. The presence of a 2,5-dichlorinated phenyl ring has been reported to facilitate degradation (2) and this is supported by the results with 2,5,2',5'-CB and 2,4,5,2',5'-CB which were degraded by 60 and 44 percent respectively.

TABLE 1. DEGRADATION OF SELECTED PCBs BY P. PUTIDA LB400*

Time (minutes)	PCB % Remaining					
	2,2'-	4,4'-	2,4,4'-	2,4,3',4'-	2,5,2',5'-	2,4,5,2',5'-
0	100	100	100	100	100	100
30	0	100	85	98	69	75
60	0	100	74	93	40	66

* Individual PCBs isomers were incubated with biphenyl-induced cells of P. putida LB400 for the times shown. PCB concentrations were determined by gas chromatography after work up as described in Materials and Methods.

DEGRADATION OF 2,2'-CB

Biphenyl-induced cells of P. putida LB400 rapidly oxidized 2,2'-CB. Most of the substrate (86%) was metabolized during the first 10 minutes of the incubation period and after 30 minutes no 2,2'-CB could be detected in the reaction mixture. Analysis of the reaction products by GC/MS revealed the presence of four metabolites with molecular ions at m/e 156, 170, 238 and 256 respectively. The identity of these compounds designated A, B, C, and D respectively are given in Table 2.

The formation of the methyl ester of 2-chlorobenzoic acid was unexpected and was attributed to the use of methanol as a solvent for 2,2'-CB. This was confirmed by repeating the experiment with 2,2'-CB dissolved in deuterated methanol (CD_3OD). The methyl ester formed gave a parent ion at M^+ 173. Nevertheless, small amounts of the methyl ester of 2-chlorobenzoic acid were detected when 2,2'-CB was added in dimethylformamide.

TABLE 2. IDENTITY OF COMPOUNDS A, B, C, AND D FORMED FROM 2,2'-CB BY *P. PUTIDA* LB400*

Compound	M^+ Cl^{35}/Cl^{37}	Structure
A	156/158	2-Chlorobenzoic acid
B	170/172	Methyl ester of 2-chlorobenzoic acid
C	238/242	2,2'-Dichlorobiphenylol†
D	256/260	Dihydrodiol derivative of 2,2'-dichlorobiphenyl†

* Products were isolated and identified by GC/MS.

† It was not possible to assign the position(s) of the hydroxyl groups in these metabolites.

In addition, methyl ester formation was not detected when 2-chlorobenzoic acid was incubated with biphenyl-induced cells of *P. putida* LB400. These results could indicate that 2-chlorobenzoic acid is not taken up by *P. putida* LB400 and that ester formation from endogenous methyl donors may be catalyzed by an intracellular enzyme.

DEGRADATION OF 2,5,2',5'-CB

Significant metabolism of 2,5,2',5'-CB was observed over a 1.0 hour time period (Table 1). At 30 min a major metabolite with a molecular ion weight of m/z 324 was detected. Over the next 30 min this compound began to disappear and was replaced with a second major metabolite (molecular weight 358). These compounds have tentatively been identified as 3,4-dihydroxy-3,4-dihydro-2,5,2',5'-tetrachlorobiphenyl and 3,4,3',4'-tetrahydroxy-3,4,3',4'-tetrahydro-2,5,2',5'-tetrachlorobiphenyl respectively. In addition to these major products small amounts of 2,5-dichloroacetophenone and a compound tentatively identified as 2,2[2',5'-dichlorophenyl] ethanol were also detected. Similar results were presented at last year's conference (9).

DEGRADATION OF 2,4,5,2',5'-CB

This pentachlorobiphenyl was rapidly oxidized by biphenyl-induced cells of *P. putida* LB400. After one hour 34% of the parent compound had disappeared and a major neutral metabolite with a retention time of 20.5 min was detected by HPLC. The exact structure of this reaction product which appears to be a phenolic metabolite has yet to be determined.

DEGRADATION OF 4,4'-CB, 2,4,3',4'-CB AND 2,4,4'-CB

Biphenyl-induced cells of *P. putida* LB400 failed to oxidize either 4,4'-CB or 2,4,3',4'-CB under the experimental conditions described in the Materials and Methods section. Even after 48 hours incubation no degradation products were detected by GC/MS. In contrast, 2,4,4'-CB was oxidized under the same conditions. The only metabolite detected by GC/MS gave a molecular ion at M^+ 272, and was tentatively identified as a phenolic derivative of 2,4,4'-CB.

ENZYMATIC OXIDATION OF BIPHENYL AND SELECTED PCBs

Cell extracts prepared from biphenyl-grown cells of *P. putida* 39/D oxidized biphenyl and the substrates shown in Table 3.

TABLE 3. OXIDATION OF BIPHENYL AND PCBs BY CELL EXTRACTS*

Substrate	Activity %
Biphenyl	100
2,2'-CB	68
4,4'-CB	0
2,5,2',5-CB	45
2,4,5,2',5'-CB	53
2,4,4'-CB	21
2,4,3',4'-CB	0
2,3,4,5',6'-CB	0

* Enzyme activity was measured polarographically as described in Materials and Methods.

DISCUSSION

The results shown in Table 1 confirm previous investigations which have shown that _P. putida_ LB400 has the capability of oxidizing a wide range of PCBs (1,3,9). However, most of these studies did not determine the rate of PCB degradation at time periods as short as one hour. When one considers that 2,2'-CB completely disappears after 30 minutes incubation with _P. putida_ LB400 whereas there is no detectable metabolism of 4,4'-CB over the same time period it seems clear that the position of the chlorine substituents plays a major role in the susceptibility of different PCB isomers and congeners to microbial degradation. In this context it is of interest to note that chlorination at the 2 position enhances the degradation of 4,4'-CB. Bedard et al. (2) have clearly shown that a 2,5-chlorination pattern enhances the degradation of certain PCB congeners and this is supported in the present study by the results obtained with 2,5,2',5'-CB and 2,4,5,2',5'-CB.

The metabolites detected as degradation products from 2,2'-CB suggest that this molecule is oxidized at the 5,6-position to form a dihydrodiol which can then be further metabolized to 2-chlorobenzoic acid. These reactions are analogous to those shown in Figure 1 for the degradation of biphenyl. However, the position of the hydroxyl groups in the dihydrodiol metabolite have not been established. It is of interest to note that a mutant strain (FM408) of _P. putida_ LB400 oxidizes biphenyl to _cis_-2,3-dihydroxy-2,3-dihydrobiphenyl. A genetic lesion in the structural gene for _cis_-2,3-dihydroxy-2,3-dihydrobiphenyl dehydrogenase causes the accumulation of the dihydrodiol metabolite (7). However when 2,2'-CB was incubated with strain FM408 the major metabolite formed was 2-chlorobenzoic acid (data not shown). Thus there may be more than one enzyme in _P. putida_ LB400 that can degrade PCBs. For example, the oxidation of 2,5,2',5'-CB at the 3,4-positions may be catalyzed by an enzyme different to that responsible for initiating the degradation of biphenyl.

A comparison of the metabolites identified in the present study with those reported in reference 5 is shown in Table 4. The failure to detect a specific metabolite does not mean that the metabolite is not formed. Thus the table reveals the limitations of the information that can be derived from whole cell studies and GC/MS analyses. We believe that more specific details of PCB degradation can be provided by studies with purified enzymes and the results shown in Table 3 represent our preliminary studies on the enzyme(s) responsible for the initial attack on the PCB ring. It is anticipated that further investigations with purified enzymes will provide more specific information on the mechanisms involved in PCB degradation.

TABLE 4. COMPARISON OF THE METABOLITES FORMED FROM SELECTED CB CONGENERS BY *P. PUTIDA* LB400, *ALCALIGENES EUTROPHUS* SP. Y42[a] AND *ACINETOBACTER* SP. P6[a]

CB isomer	Dihydro-diol	Dihydroxy compound	Chloroben-zoate	Other
2,2'-	■[b]--	-[c]-o[d]	x[e]o	monohydroxy compound (■) benzoic acid methyl ester (■)
4,4'-	- x -	- - -	- x o	-
2,4,4'-	- - o	- - o	- x o	monohydroxy compound (■,o)
2,5,2',5'-	- -	- - o	- - -	2,5-dichloroacetophenone (■) 2,2[2',5'-dichlorophenyl] ethanol (■)
2,4,3',4'-	- - -	- - -	- - o	monohydroxy compound (o)
2,4,5,2',5'-[f]	- - -	- - o	- - -	monohydroxy compound (o)

a Data taken from reference 5
b *P. putida* LB400 (■)
c none detected
d *Acinetobacter* sp. P6 (o)
e *Alcaligenes* sp. Y42 (x)
f metabolites formed but not identified

ACKNOWLEDGMENTS

This work was supported by grant CR812727 from the Office of Research and Development, the Environmental Protection Agency. We thank Dr. P.R. Sferra, EPA Project Officer for his interest and suggestions. We thank Catherine Potter for her patience and skill in organizing and typing the manuscript.

REFERENCES

1. Bedard, D.L., Unterman, R., Bopp, L.H., Brennan, M.J., Haberl, M.L. and Johnson, C. Rapid assay for screening and characterizing microorganisms for the ability to degrade polychlorinated biphenyls. *Appl. Environ. Microbiol.* 51: 761, 1986.

2. Bedard, D.L., Haberl, M.L., May, R.J. and Brennan, M.J. Evidence for novel mechanisms of polychlorinated biphenyl metabolism in Alcaligenes eutrophus H850. Appl. Environ. Microbiol. 53: 1103, 1987.

3. Bopp, L.H. Degradation of highly chlorinated PCBs by Pseudomonas strain LB400. J. Ind. Microbiol. 1: 23, 1986.

4. Brown, J.F., Jr., Bedard, D.L., Brennan, M.J., Carnahan, J.C., Feng, H. and Wagner, R.E. Polychlorinated biphenyl degradation in aquatic sediments. Science 236: 709, 1987.

5. Furukawa, K., Tomizuka, N., Kamibayashi, A. Effect of chlorine substitution on the bacterial metabolism of various polychlorinated biphenyls. Appl. Environ. Microbiol. 38: 301, 1979.

6. Furukawa, K. Microbial degradation of polychlorinated biphenyls (PCBs) In: A.M. Chakrabarty (ed.), Biodegradation and Detoxification of Environmental Pollutants. CRC Press, Boca Raton, Florida, 1982. p. 33.

7. Gibson, D.T., Roberts, R.L., Wells, M.C. and Kobal, V.M. Oxidation of biphenyl by a Beijerinckia sp. Biochem. Biophys. Res. Commun. 50: 211, 1973.

8. Hutzinger, O.H.O., Safe, S.H., Zitko, V. Commercial PCB preparations, properties and composition. In: The Chemistry of PCBs. CRC Press, Cleveland, Ohio, 1974. p. 8.

9. Nadim, L.M., Schocken, M.J., Higson, F.K., Gibson, D.T., Bedard, D.L., Bopp, L.H. and Mondello, F.J. Bacterial oxidation of polychlorinated biphenyls. In: Proceedings of the Second International Conference on New Frontiers for Hazardous Waste Management. U.S.E.P.A., Cincinnati 1987. p. .

10. Safe, S.H. Microbial degradation of polychlorinated biphenyls. In: D.T. Gibson (ed.), Microbial Degradation of Organic Compounds. Marcel Dekker, Inc., New York, 1984. p. 361.

Biological Oxidations of Organic Compounds by Enzymes from a White Rot Fungus

by: J.A. Bumpus, G. Mileski, B. Brock, W. Ashbaugh,
S.D. Aust
Biotechnology Center
Utah State University
Logan, UT 84322-4430

ABSTRACT

The ability of the white rot fungus Phanerochaete chrysosporium to degrade a wide variety of structurally diverse organopollutants is dependent upon the lignin degrading system of this microorganism. In part, the lignin degrading system consists of a family of peroxidases, which are able to catalyze the initial oxidative depolymerization of lignin. In addition, these enzymes catalyze the initial oxidation of many "hard-to-degrade" xenobiotics. Current research is focused on ways to increase ligninase activity in culture and on understanding the enzymology of this system as it affects xenobiotic oxidation. Ligninase activity is expressed by the fungus in response to nutrient nitrogen limiting conditions. In agitated cultures (1 L total volume in 2.8 L Fernbach flasks), ligninase activities up to 446 units (μmoles of veratryl alcohol oxidized) per liter, representing approximately a 20-fold increase over standard stationary cultures, were observed. Furthermore, ligninase activity was shown to be cyclic, reaching peak activities at about 30 hour intervals. Substantial ligninase activity (200 units/liter) was also observed in 100 ml stationary cultures containing 1.5 mM veratryl alcohol representing approximately a 10 fold increase over standard stationary cultures. In these cultures, veratryl alcohol may serve to induce ligninase biosynthesis and/or it may protect the enzyme from subsequent inactivation. Ligninase H-2 was the predominant or second most predominant ligninase isozyme produced in culture and was purified to electrophoretic homogeneity by Fast Protein Liquid Chromatography (FPLC). In addition to veratryl alcohol oxidation (oxidation of a benzylic carbon), ligninase H-2 catalyzed the oxidative dechlorination of pentachlorophenol (PCP) to form 2,3,5,6-tetrachloro-2,5-cyclohexadiene-1,4-dione, N-demethylation of crystal violet to form N,N,N',N',N"-pentamethylpararosaniline and the oxidation of pyrene, presumably forming the quinones of this polycyclic aromatic hydrocarbon.

INTRODUCTION

The ability of the white rot fungus Phanerochaete chrysosporium to degrade a wide variety of structurally diverse organopollutants to carbon dioxide has been shown to be dependent upon the lignin degrading system of this fungus, that is expressed under idiophasic conditions (1-8) as a consequence of nutrient (nitrogen, carbon or sulfur) limitation (1-10). In part, the lignin degrading system consists of a family of enzymes, commonly referred to as ligninases, that are able to catalyze the oxidative depolymerization of lignin (11,12). Following depolymerization, the smaller and more water soluble lignin-derived metabolites may be further modified by these enzymes or by a family of manganese-dependent peroxidases that are also secreted by the fungus during idiophasic metabolism (13-15). The lignin degrading system also contains an aromatic ring cleavage system (16). It is unclear at present whether or not cleavage of the aromatic ring moieties of lignin, in vivo, takes place before, after or during lignin depolymerization. However, regardless of this, it is apparent that aromatic ring cleavage of many different low molecular weight compounds readily occurs in ligninolytic cultures of this fungus (1-8,16). Intermediates of lignin and xenobiotic degradation are metabolized to Krebs cycle intermediates and, eventually, to carbon dioxide to complete the mineralization process.

The enzymology and protein chemistry of ligninases has been the subject of considerable attention since their discovery in 1983 (11,17). It is known that ligninases are more properly known as lignin peroxidases in that they contain protoporphyrin IX as a prosthetic group and form intermediates similar to the compound I and compound II intermediates of other peroxidases (18,19,20). All ligninases characterized to date are glycoproteins having molecular weights between 38,000 and 46,000 (19). Ligninase isozymes are designated as H-1 through H-10. The letter H refers to the fact that the isozyme in question is a heme-protein while the number designates the order in which the isozyme elutes from a mono Q (Pharmacia, Uppsala, Sweden) anion exchange column during Fast Protein Liquid Chromatography (21). To date most research has been performed using ligninase H-8, the most abundant ligninase expressed in standard stationary cultures of P. chrysosporium. This enzyme is able to catalyze benzylic alcohol oxidation, carbon-carbon bond cleavage, hydroxylation, phenol dimerization and O-demethylation of lignin model compounds (12). A complementary DNA (cDNA) of ligninase H-8 has also been cloned and expressed in Escherichia coli and the cloned cDNA has been sequenced revealing the primary amino acid sequence of ligninase H-8 (22).

Less attention has been focused on the biodegradation of environmental pollutants by ligninases. However, it has been shown that ligninase H-8 is able to oxidize benzo[a]pyrene as well as a number of other polyaromatic hydrocarbons. In the case of benzo[a]pyrene, the benzo[a]pyrene 1,6-, 3,6- and 6,12-quinones are formed (23) whereas pyrene is oxidized to the pyrene-1,6- and 1,8-diones (24). Dibenzo[p]dioxin and 2-chlorodibenzo[p]dioxin are also oxidized by ligninase H-8 (24). Of importance is the fact that ligninase catalyzed oxidation of dibenzo[p]dioxin occurs via a cation radical intermediate (24) as is observed during the degradation of lignin model compounds (25). This suggests that the non-specific free radical mechanisms active in lignin biodegradation are operative in ligninase-catalyzed oxidation of environmental pollutants (24).

The use of P. chrysosporium and its biodegradative enzymes for the treatment of organochemical wastes holds considerable potential. However, a more thorough understanding of the enzymology of biodegradation as it occurs in this fungus is required if this potential is to be fully realized. The present study focuses on the production of ligninases in cultures of P. chrysosporium. It also describes the purification and characterization of ligninase H-2 with special attention to its ability to oxidize several model organopollutants.

METHODS AND MATERIALS

MICROORGANISM

Phanerochaete chrysosporium (BKM-F-1767) was obtained from the United States Department of Agriculture, Forest Products Laboratory (Madison, WI) and maintained on malt agar slants at room temperature. Subcultures were routinely made every 30-60 days.

CULTURE CONDITIONS

P. chrysosporium was incubated at 37°C in the liquid culture medium (10 ml) previously described (26) in 250 ml Wheaton bottles equipped with caps having a Teflon seal. This medium consists of 56 mM glucose, 1.2 mM ammonium tartrate, mineral salts and thiamine (1 mg/L) in 20 mM dimethylsuccinate (sodium) buffer, pH 4.5. Cultures were established by inoculating the medium with spores as described (27). During the first three days of incubation, cultures were allowed to grow in an atmosphere of air. After three days, the cultures were grown in an atmosphere of 100% oxygen. Under these conditions, which are referred to as "basal conditions", ligninase activities of 15-20 μmoles/L were obtained after 5-6 days of incubation. P. chrysosporium was also cultured in 100 ml of the basal media supplemented with 1.5 mM veratyl alcohol in 2.8 L Fernbach flasks. As with the 10 ml stationary cultures, these cultures were grown under an atmosphere of air for the first three days after which they were grown under an atmosphere of 100% oxygen. Large scale (1 L) agitated cultures of P. chrysosporium were also used. Agitated cultures were initiated from two day old mat cultures as described (28) except that the culture medium of the mat cultures consisted of 10 mM dimethylsuccinate (sodium), pH 4.5, containing 56 mM glucose, 1.2 mM ammonium tartrate, thiamine and a mineral supplement (27) and the cultures were grown under ambient atmosphere rather than 100% oxygen. The agitated culture medium consisted of 10 mM dimethylsuccinate (sodium), pH 4.5 containing 56 mM glucose, 1.2 mM ammonium tartrate, 0.4 mM veratryl alcohol, 0.6 mM benzyl alcohol, 0.1% Tween 80, thiamine (1 mg/L) and a mineral supplement that was 7 fold the concentration of that used in the mat culture (27). Cultures were incubated on an incubator shaker (200 rpm) at 37°C.

LIGNINASE PURIFICATION

Ligninase H-2 was purified from the extracellular fluid of agitated (1 L) or stationary (100 ml) cultures of P. chrysosporium by Fast Protein Liquid Chromatography using procedures similar to those previously described (28). Briefly, purification procedures entailed the harvesting of the extracellular fluid of ligninolytic cultures of P. chrysosporium followed by concentration using a Millipore Minitan concentrator equipped with a filter with a molecular exclusion limit of 10,000. The preparation was then frozen, thawed and centrifuged (15,000 xg, 20 min) twice in order to remove mucilaginous material that interfered with subsequent chromatography. The preparation was then dialyzed overnight against 10 mM sodium acetate, pH 6.0, and the ligninases were purified by FPLC using a Mono Q HR 10/10 column (Pharmacia, Uppsala, Sweden). The sample was applied in 10 mM sodium acetate, pH 6.0, and washed with 25 ml of the same buffer. The column was eluted with a linear gradient from 10 mM sodium acetate, pH 6.0, to 0.7 M sodium acetate, pH 6.0 (2 ml/min, 70 min). Ligninase H-2 eluted at 0.18 M sodium acetate. This peak was collected and stored at -20°C until used.

ENZYME ASSAYS

Ligninase activity (veratryl alcohol oxidase activity) was measured by the procedure described by Tien and Kirk (12). One unit of enzyme activity oxidized one μmol of veratryl alcohol in one minute at room temperature. Oxidation of pyrene by ligninase H-2 was assayed as described for ligninase H-8 (24). Oxidation of crystal violet was assayed by monitoring the decrease in absorption at 591 nm, its visible wavelength maximum. The reaction mixture contained crystal violet (2 μM - 25 μM), 50 mM sodium succinate buffer, pH 4.5, and 20 μM or 400 μM H_2O_2. Metabolites of crystal violet oxidation were separated by High Performance Liquid Chromatography (HPLC). Following incubation, 0.5 ml aliquots of the reaction mixture were extracted with 0.5 ml of methylene chloride and 50 μl aliquots of the methylene chloride extracts were used for HPLC analysis.

Reverse phase HPLC was performed using a system equipped with an Altex model 110A pump (Anspec Co., Inc., Ann Arbor, MI), a Rheodyne injector (Rheodyne, Inc., Cotati, CA), an R-Sil C-18 reverse phase column (4.6 x 250 mm) (Alltech Associates Inc., Deerfield, IL) and a Schoeffel Model 770 detector (ABI Analytical, Kratos Div., Ramsey, NJ). Isocratic elution was performed using acetonitrile/water (80/20) containing 0.01 M 2-naphthalenesulfonic acid and 0.01 M trifluoroacetic acid as described (29). Elution was monitored at 560 nm. Crystal violet and its metabolites (N,N,N',N',N"-pentamethylpararosaniline, N,N,N',N"-tetramethylpararosaniline and N,N',N"-

trimethylpararosaniline) were identified by comigration with authentic standards.

PCP oxidation was assayed by monitoring the increase in absorption at 266.5 nm. The reaction mixture contained 20 mM sodium tartrate pH 3.0, 20 μM H_2O_2, 20 μM PCP and 25 nM ligninase H-2. The reaction was initiated by addition of H_2O_2. Metabolites of PCP oxidation were separated by HPLC. PCP and PCP metabolites were extracted from aliquots (10 ml) of the reaction mixture with hexane (1 ml). HPLC was performed using the Beckman System Gold HPLC equipped with an Econosphere (Alltech Associates Inc., Deerfield, IL) reversed phase (C-18) column (4.6 mm x 250 mm). Isocratic elution was performed using acetonitrile:H_2O:glacial acetate acid (75:25:0.125). Elution of PCP and its metabolite were monitored at 238 nm and 290 nm, respectively.

RESULTS AND DISCUSSION

ENHANCED PRODUCTION OF LIGNINASES

Ligninases have been shown to catalyze the oxidative depolymerization of lignin (11) as well as the initial oxidation of certain xenobiotics (22,23). The initial oxidation of many compounds is oftentimes the most difficult one and, in some cases, may be rate limiting. Therefore, a logical approach to increasing the biodegradative abilities of this fungus would be to increase net production of ligninases. Although it is, conceptually, a straight forward approach, in practice it is not necessarily easy to scale up ligninase production from the 10 ml cultures used in many laboratories (19). Ligninase activity appears to depend upon oxygen partial pressure (19). It also depends upon culture and flask volume (19). Thus increased culture and flask volume does not necessarily result in a proportionate increase in ligninase activity (19). Increased production of ligninases by altering the incubation conditions has been reported, however, by several research groups. For example, Leisola _et_ _al_. (30) reported that 1-2 mM veratryl alcohol added to nitrogen limited stationary and carbon limited agitated cultures of _P. chrysosporium_ BKM-F-1767 resulted in veratryl alcohol oxidase (ligninase) activities up to 180 and 670 units/liter, respectively. Similarly, Jager _et_ _al_. (28) reported that ligninase activities as high as 131-144 units/liter could be achieved in agitated cultures supplemented with 0.05-0.1% Tween 80, 0.4 mM veratryl alcohol and increased (7X) levels of trace elements. The highest levels of ligninase activity reported to date are those of Asther _et_ _al_. (31) who used a different strain of _P. chrysosporium_ (INA-12). These investigators reported ligninase activities of 1,344 units/L and 1,158 units/L in stationary and agitated cultures, respectively, supplemented with oleic acid emulsified with Tween 80 (0.04%, w/v). Most recently, Kirkpatrick and Palmer (32) developed conditions whereby _P. chrysosporium_ BKM-F-1767 immobilized on polyurethane foam enabled ligninases to be produced in high amounts (550-950 units/liter) on a semi-continuous basis.

We have also investigated ways to increase ligninase production. Using culture conditions similar to those reported by Jager et al. (28), we have been successful in achieving ligninase concentrations as high as 446 units/liter in agitated cultures of P. chrysosporium BKM-F-1767. We also showed that under these conditions, ligninase production was cyclic (Figure 1) with peak ligninase activity occurring at about 30 hour intervals following the initial ligninase peak. These results are significant because they show that in order to maximize ligninase production methods, ligninase activity must be monitored at frequent intervals so that cultures may be harvested at peak ligninase activity.

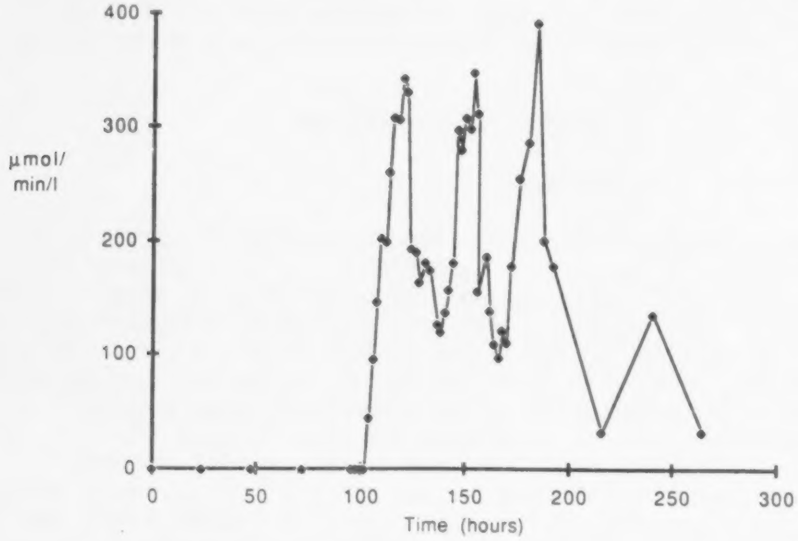


Figure 1. Ligninase activity in agitated cultures of P. chrysosporium. Cultures (1 L) were incubated in 2.8 L Fernbach flasks on a rotary shaker (200 rpm) at 37°C as described in Methods and Materials. After its onset, ligninase activity was monitored at 2 hr intervals.

We have also investigated ways to enhance ligninase production in stationary 100 ml cultures. Our results were similar to those of Leisola et al. (30) in that the addition of 1.5 µM veratryl alcohol resulted in cultures containing a 9-10 fold increase of ligninase activity relative to basal conditions.

OXIDATION OF XENOBIOTICS BY LIGNINASES FROM P. chrysosporium

It is now known that P. chrysosporium has remarkable biodegradative abilities. In addition to its ability to degrade naturally occurring biopolymers, it is known that this fungus has the ability to degrade a wide variety of chlorinated and nonchlorinated environmental pollutants as well as many other compounds. Table I is a summary of the chemicals reported to be degraded by P. chrysosporium.

Most biodegradation studies using P. chrysosporium have been performed using the organism in culture (1-8). These studies suggested that enzymes involved in ligninase degradation were also involved in xenobiotic degradation and recent evidence (23,24) has shown this hypothesis to be correct. As noted above, ligninase H-8 has been shown to oxidize dibenzo[p]dioxin, 2-chlorodibenzo[p]dioxin, benzo[a]pyrene and pyrene as well as a number of other polycyclic aromatic hydrocarbons (PAH) (23,24). An interesting facet of the results of Hammel et al. (24) is the observation that ligninase H-8 is able to oxidize PAH with ionization potentials up to ~7.55 eV whereas the well-studied horseradish peroxidase is unable to oxidize PAH with ionization potentials greater than 7.35 eV. This is the basis for the suggestion that the H_2O_2 oxidized intermediates of lignin peroxidases (compound I and II) are more electropositive (i.e., better oxidants) than comparable intermediates of other peroxidases. It was also shown that PAH compounds with ionization potentials higher than ~7.55 eV were not oxidized by ligninase H-8. This is interesting because we have shown (5) that phenanthrene, which has an ionization potential greater than 8.0 eV (33,34), is mineralized by P. chrysosporium, thus suggesting that other enzymes, possibly other ligninases, may exist in P. chrysosporium that have even greater oxidative capacities than the well-studied ligninase H-8.

In the present study, we purified ligninase H-2 from nitrogen-limited cultures of P. chrysosporium and partially characterized the isozyme with special regard to its ability to oxidize several xenobiotics. The molecular weight of this hemeprotein was estimated to be approximately 41,000. H_2O_2 was required as an oxidizing co-substrate. The specific activity of the enzyme was variable from preparation to preparation. An average specific activity of 39.9 ± 16.1 (N = 6) units/min/mg was observed.

In addition to veratryl alcohol, ligninase H-2 oxidized pentachlorophenol, crystal violet, and pyrene (Figures 2, 3, 5). These chemicals were selected as "model" compounds for several reasons. For example, pentachlorophenol (PCP) has been widely used as a wood preservative, is an acknowledged toxic environmental pollutant, and is relatively resistant to microbial degradation (35). Although crystal violet is not considered to be as great an environmental problem as PCP or PAH, it is used as a biological stain, as a topical treatment in human and veterinary medicine, and is used as a dye (36). It is not considered to be carcinogenic. However, crystal violet has been shown to be a potent clastogen (37,38) and it is toxic to many bacteria, a fact that makes its biodegradation difficult in the environment and in waste treatment systems (39). Pyrene was chosen as a representative PAH. Although pyrene itself is non-mutagenic, many PAH are mutagenic, carcinogenic and environmentally persistent (40). Pyrene is found in creosote (41), a PAH mixture derived from coal tar that has seen extensive use as a wood preservative. Pyrene has also been shown to be oxidized by ligninase H-8 (24).

TABLE I. ORGANIC COMPOUNDS DEGRADED BY *P. CHRYSOSPORIUM*

Polycyclic Aromatic Compounds
- Benzo[a]pyrene
- Biphenyl
- 2-Methylnaphthalene
- Phenanthrene
- Benzo[a]anthracene
- Pyrene
- Anthracene
- Perylene
- Dibenzo[p]dioxin

Chlorinated Aromatic Compounds
- 4-Chlorobenzoic Acid
- Dichlorobenzoic Acid
- 2,4,6-Trichlorobenzoic Acid
- 4,5-Dichloroguaiacol
- 6-Chlorovanillin
- 4,5,6-Trichloroguaiacol
- Tetrachloroguaiacol
- Pentachlorophenol
- 3-Chloroaniline
- 3,4-Dichloroaniline
- 2,4,5-Trichlorophenoxyacetic acid

Polycyclic Chlorinated Aromatic Compounds
- DDT (1,1,1-trichloro-2,2-bis(4-chlorophenyl)ethane
- 2,3,7,8-Tetrachlorodibenzo-p-dioxin
- 3,4,3',4'-Tetrachlorobiphenyl
- 2,4,5,2',4',5'-Hexachlorobiphenyl
- Aroclor 1254
- Aroclor 1242
- 2-Chlorodibenzo[p]dioxin
- Dicofol (2,2,2-trichloro-1,1-bis(4-chlorophenyl)ethanol

Chlorinated Alkyhalides
- Lindane
- Chlordane

Biopolymers
- Lignin
- Cellulose
- Kraft Lignin
- 3-chloroaniline-lignin conjugate
- 3,4-dichloroaniline-lignin conjugate

Triphenylmethane Dyes
- Crystal violet
- Pararosaniline
- Cresol red
- Bromphenol blue
- Ethyl violet
- Malachite green
- Brilliant green

The above is a partial list of compounds degraded by *P. chrysosporium* compiled from ref. 1, 3, 4, 5, 7, 8, 23, 24, 44 and from unpublished observations in our laboratory.

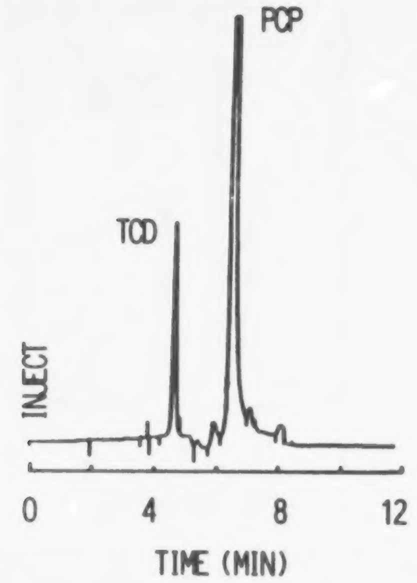


Figure 2. Reversed phase HPLC of the products of PCP oxidation by ligninase H-2. Conditions were as described under Methods and Materials. Product (2,3,5,6-tetrachloro-2,5-cyclohexadiene-1,4-dione(TCD)) was identified by comigration with an authentic standard.

Figure 2 shows that PCP was oxidized by ligninase H-2. HPLC analysis of enzyme reaction mixtures showed that PCP underwent oxidation and dechlorination at C-4 to form 2,3,5,6-tetrachloro-2,5-cyclohexadiene-1,4-dione. This is important because it demonstrates that at least one enzyme from P. chrysosporium has the ability to catalyze dechlorination of chlorinated organic compounds. It has been known for some time that certain bacteria and fungi degrade PCP and that the pathway involves dechlorination and hydroxylation either ortho or para to the hydroxyl group to form a catechol or quinone (or hydroquinone) (42). However, until now, no bacterial or fungal enzyme has been shown to catalyze either of these reactions (42).

Figure 3 shows the separation of crystal violet and its metabolites by HPLC following incubation with ligninase H-2 and H_2O_2. Three products were identified as N,N,N',N',N"-pentamethylpararosaniline, N,N,N',N"-tetramethylpararosaniline and N,N',N"-trimethylpararosaniline. These results indicate that the initial step in the biodegradation of crystal violet by P. chrysosporium is the N-dealkylation of crystal violet to form N,N,N',N',N"-pentamethylpararosaniline which may then undergo subsequent N-demethylation to form N,N,N',N"-tetramethylpararosaniline which may also serve as a substrate to form N,N',N"-trimethylpararosaniline. H_2O_2 irreversibly inactivated the enzyme during crystal violet oxidation. Results (Figure 4) indicated that in addition to being a required oxidizing substrate, H_2O_2 is also a competitive inhibitor. This interpretation is

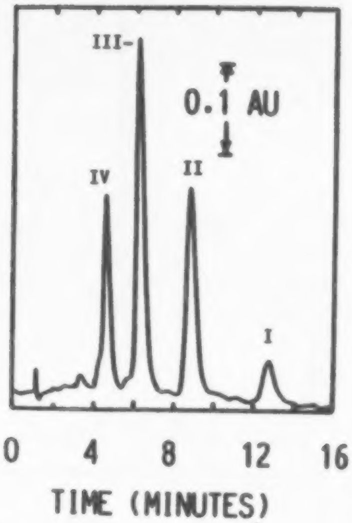


Figure 3. Reversed phase HPLC of the products of crystal violet oxidation by ligninase H-2. Peaks I, II, III and IV were identified as crystal violet (N,N,N',N',N",N"-hexamethylpararosaniline), N,N,N',N',N"-pentamethylpararosaniline, N,N,N',N"-tetramethylpararosaniline, and N,N',N"-trimethylpararosaniline, respectively. Product identifications were made on the basis of comigration with authentic standards.

supported by the data in Figure 4 which show that increasing amounts of the reducing co-substrate (crystal violet) abolished the inhibitory effects of high concentrations of H_2O_2.

The PAH pyrene was also shown to be oxidized by ligninase H-2 (Figure 5). These results are similar to those of Hammel et al. (24) who, as noted above, showed that pyrene is oxidized by ligninase H-8.

These results, together with others in the literature, show that ligninases purified from P. chrysosporium are able to catalyze an impressive array of biological oxidations of xenobiotics. Included among the reactions catalyzed are: 1, the oxidation of PAH; 2, oxidative dechlorination of chlorophenols; 3, oxidation of dibenzo[p]dioxin and 2-chlorodibenzo[p]dioxin; and 4, N-dealkylation of arylamines.

OTHER CONSIDERATIONS

In addition to results obtained with pure enzyme, considerable indirect evidence exists concerning the enzymatic capabilities of this microorganism. For example, it is known that in cultures of P. chrysosporium dicofol and DDT both undergo reductive dechlorination of their chlorine bearing alkyl carbon to form FW-152 and DDD, respectively (1,3). It is also known that

DDT undergoes benzylic carbon hydroxylation to form dicofol (1,3) and that FW-152 and dicofol undergo cleavage between C-1 and C-2 to form DBP (3). It is also apparent that P. chrysosporium must possess an enzyme system able to catalyze aromatic ring cleavage of xenobiotic metabolites as evidenced by the fact that many xenobiotics that are ^{14}C-labeled in the aromatic ring(s) are degraded to $^{14}CO_2$ by this fungus (1-8). The mechanisms involved in the above reactions and the extent to which ligninases catalyze these reactions is the subject of ongoing research in this laboratory.

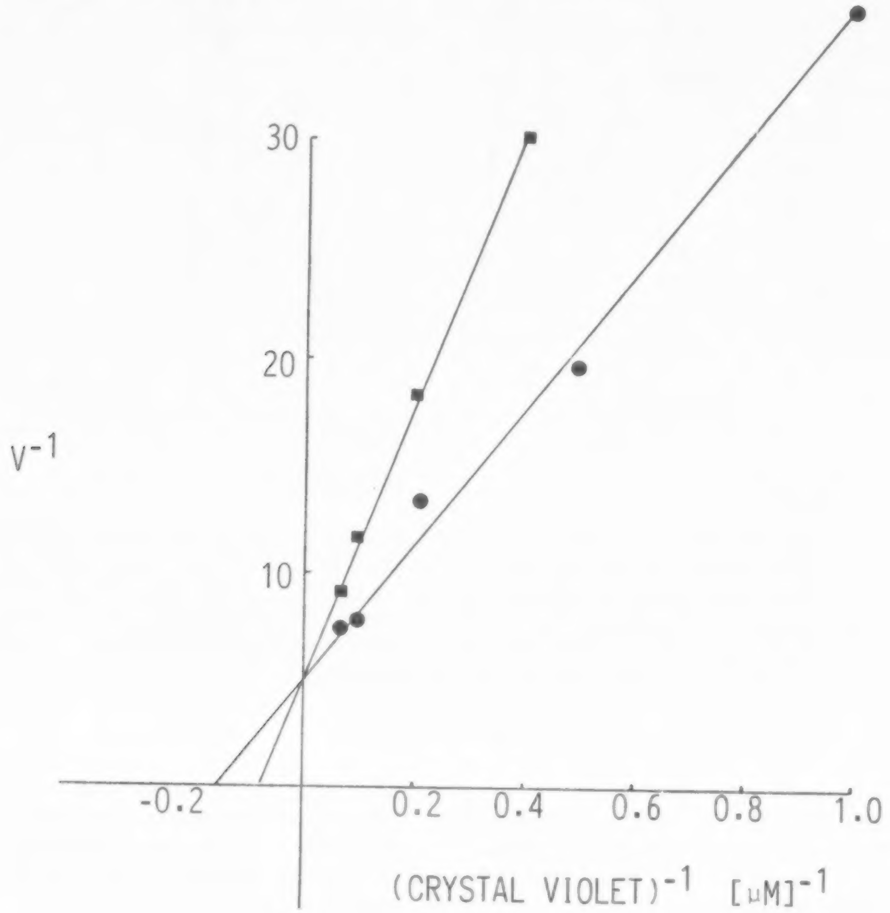


Figure 4. Effect of H_2O_2 on the initial velocity of crystal violet oxidation by ligninase H-2 as a function of crystal violet concentration. The reaction mixtures (1.0 ml) contained either 20 μM (Closed circles) or 400 μM (Closed squares) H_2O_2, 2.0 μg ligninase H-2, and variable amounts of crystal violet in 50 mM sodium succinate, pH 4.5. Reactions were performed at room temperature and were initiated with H_2O_2.

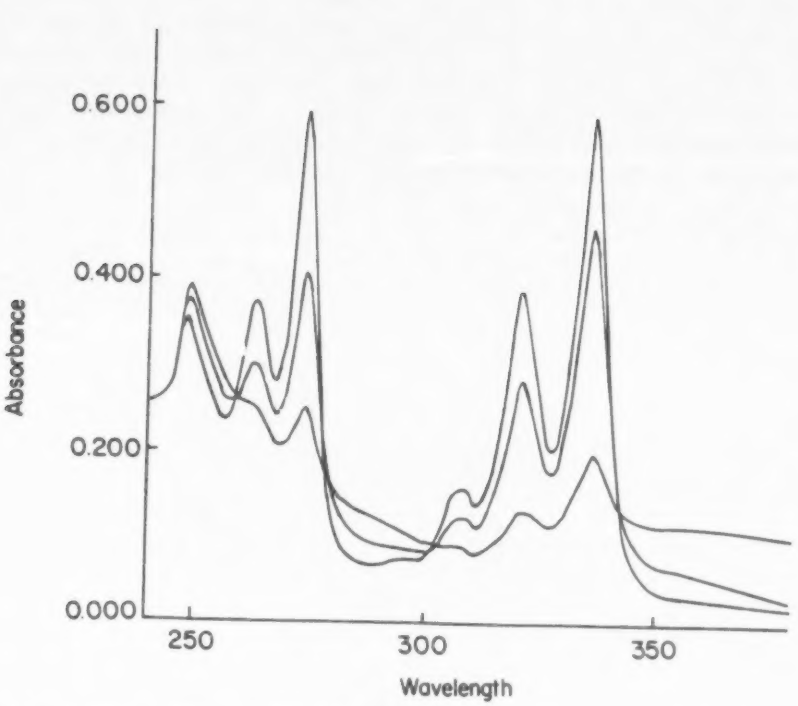


Figure 5. Oxidation of pyrene by ligninase H-2. The reaction mixture contained 20 μM pyrene, 8.54 μg ligninase H-2, and 200 μM H_2O_2 in H_2O/N,N-dimethylformamide 8:2 containing 20 mM sodium tartrate, pH 2.5. The reaction, which was initiated with H_2O_2, was scanned between 240 nm and 380 nm prior to addition of H_2O_2, immediately after addition and after 14 minutes.

ACKNOWLEDGEMENTS

This work was supported by Cooperative Agreement CR-814448 from the Hazardous Waste Engineering Laboratory, Office of Research and Development, U.S. Environmental Protection Agency, Cincinnati, Ohio, P.R. Sferra, project officer. The authors thank Terri Maughan for her expert secretarial assistance and Toni Patik for technical assistance.

REFERENCES

1. Bumpus, J.A., Tien, M.. Wright, D., and Aust, S.D. Oxidation of persistent environmental pollutants by a white rot fungus. Science 228: 1434, 1985.

2. Bumpus, J.A. and Aust, S.D. Biodegradation of environmental pollutants by the white rot fungus Phanerochaete chrysosporium: Involvement of the lignin degrading system. BioEssays 6: 166, 1987.

3. Bumpus, J.A. and Aust, S.D. Biodegradation of DDT (1,1,1-Trichloro-2,2-Bis(4-Chlorophenyl)Ethane) by the white rot fungus *Phanerochaete chrysosporium*. Appl. Environ. Microbiol. 59: 2001, 1987.

4. Bumpus, J.A. and Aust, S.D. Biodegradation of chlorinated organic compounds by *Phanerochaete chrysosporium*, a wood-rotting fungus. *In*: Solving Hazardous Waste Problems: *Learning From Dioxins* (Jurgen H. Exner, ed.). ACS Symposium Series 338, American Chemical Society, Washington, D.C., 1987.

5. Bumpus, J.A. and Aust, S.D. Mineralization of recalcitrant environmental pollutants by a white rot fungus. Proceedings of the National Conference on Hazardous Wastes and Hazardous Materials. Hazardous Materials Control Research Institute, Silver Spring, MD. Library of Congress Catalog No. 87-80469, 1987. p. 146.

6. Sanglard, D., Leisola, M.S.A., and Fiechter, A. Role of extracellular ligninases in biodegradation of benzo[a]pyrene by *Phanerochaete chrysosporium*. Enzyme Microb. Technol. 8: 209, 1986.

7. Arjmand, M. and Sandermann, Jr., H. Mineralization of chloroaniline/lignin conjugates and of free chloroanilines by the white rot fungus *Phanerochaete chrysosporium*. J. Agric. Food Chem. 33: 1055, 1985.

8. Eaton, D.C. Mineralization of polychlorinated biphenyls by *Phanerochaete chrysosporium*: a ligninolytic fungus. Enzyme Microb. Technol. 7: 194, 1985.

9. Jeffries, T.W., Choi, S., and Kirk, T.K. Nutritional regulation of lignin degradation by *Phanerochaete chrysosporium*. Appl. Environ. Microbiol. 42: 290, 1981.

10. Leisola, M.S.A., Kozulic, B., Meussduerffer, F., and Fiechter, A. Homology among multiple extracellular peroxidases from *Phanerochaete chrysosporium*. J. Biol. Chem. 262: 419, 1987.

11. Tien, M. and Kirk, T.K. Lignin-degrading enzyme from the Hymenomycete *Phanerochaete chrysosporium* Burds. Science 221: 661, 1983.

12. Tien, M. and Kirk, T.K. Lignin-degrading enzyme from *Phanerochaete chrysosporium*: purification, characterization and catalytic properties of a unique H_2O-requiring oxygenase. Proc. Natl. Acad. Sci. 81: 2280, 1984.

13. Kuwahara, M., Glenn, J.K., Morgan, M.A., and Gold, M.H. Separation and characterization of two extracellular H_2O_2-dependent oxidases from ligninolytic cultures of *Phanerochaete chrysosporium*. FEB Letters 169: 247, 1984.

14. Glenn, J.K., Akileswaran, L., and Gold, M.H. Mn(II) oxidation is the principal function of the extracellular Mn-peroxidase from *Phanerochaete chrysosporium*. Archives Biochem. Biophys. 251: 688, 1986.

15. Paszczynski, A., Huynh, V.-B., and Crawford, R.L. Comparison of ligninase-I and peroxidase M-2 from the white rot fungus *Phanerochaete chrysosporium*. Arch. Biochem. Biophys. 244: 750, 1985.

16. Leatham, G.F., Crawford, R.L., and Kirk, T.K. Degradation of phenolic compounds and ring cleavage of catechol by *Phanerochaete chrysosporium*. Appl. Environ. Microbiol. 46: 191, 1983.

17. Glenn, J.K., Morgan, M.A., Mayfield, M.B., Kuwahara, M., and Gold, M.H. An extracellular H_2O_2-requiring enzyme preparation in lignin biodegradation by the white rot basidiomycete *Phanerochaete chrysosporium*. Biochem. Biophys. Res. Comm. 114: 1077, 1983.

18. Renganathan, V. and Gold, M.H. Spectral characterization of the oxidized states of lignin peroxidase, an extracellular heme enzyme from the white rot basidiomycete *Phanerochaete chrysosporium*. Biochem. 25: 1626, 1986.

19. Tien, M. Properties of ligninase from *Phanerochaete chrysosporium* and their possible applications. CRC Critical Reviews in Microbiology 15: 141, 1987.

20. Andrawis, A., Johnson, K.A., and Tien, M. Studies on compound I formation of the lignin peroxidase from *Phanerochaete chrysosporium*. J. Biol. Chem. 263: 1195, 1988.

21. Kirk, T.K., Croan, S., Tien, M., Murtagh, K.E., and Farrell, R.L. Production of multiple ligninases by *Phanerochaete chrysosporium*: Effect of selected growth conditions and use of a mutant strain. Enzyme Microb. Technol. 8: 27, 1986.

22. Tien, M. and Tu, C.-P.D. Cloning and sequencing of a cDNA from a ligninase from *Phanerochaete chrysosporium*. Nature 326: 520, 1987.

23. Haemmerli, S.D., Leisola, M.S.A., Sanglard, D., and Fiechter, A. Oxidation of benzo[a]pyrene by extracellular ligninases of *Phanerochaete chrysosporium*: Veratryl alcohol and stability of ligninase. J. Biol. Chem. 261: 6900, 1986.

24. Hammel, K.E., Kalyanaraman, B., and Kirk, T.K. Oxidation of polycyclic aromatic hydrocarbons and dibenzo[p]dioxins by *Phanerochaete chrysosporium* ligninase. J. Biol. Chem. 261: 16948, 1986.

25. Hammel, K.E., Tien, M., Kalyanaraman, B., and Kirk, T.K. Mechanism of oxidative C_α-C_β cleavage of a lignin model dimer by Phanerochaete chrysosporium ligninase: Stoichiometry and involvement of free radicals. J. Biol. Chem. 260: 8348, 1985.

26. Fenn, P. and Kirk, T.K. Ligninolytic system of Phanerochaete chrysosporium: Inhibition by o-phthalate. Arch. Microbiol. 123: 307, 1979.

27. Kirk, T.K., Schultz, E., Connors, W.J., Lorenz, L.F., and Zeikus, J.G. Influence of culture parameters on lignin metabolism by Phanerochaete chrysosporium. Arch. Microbiol. 117: 277, 1978.

28. Jager, A., Croan, S., and Kirk. T.K. Production of ligninases and degradation of lignin in agitated submerged cultures of Phanerochaete chrysosporium. Appl. Environ. Microbiol. 50: 1274, 1985.

29. Abidi, S.L. High-performance liquid chromatography of quinoidal imminium compounds derived from triphenylmethanes. J. Chromatog. 255: 101, 1983.

30. Leisola, M.S.A., Thanei-Wyss, U., and Fiechter, A. Strategies for production of high ligninase activities by P. chrysosporium. J. Biotechnol. 3: 97, 1985.

31. Asther, M., Corrieu, G., Drapron, R., and Odier, E. Effect of Tween 80 and oleic acid on ligninase production by Phanerochaete chrysosporium INA-12. Enzyme Microb. Technol. 9: 245.

32. Kirkpatrick, N. and Palmer, J.M. Semi-continuous ligninase production using foam-immobilized Phanerochaete chrysosporium. Appl. Microbiol. Biotechnol. 27: 129, 1987.

33. Pysh, E.S. and Yang, N.C. Polarographic oxidation potentials of aromatic compounds. J. Am. Chem. Soc. 85: 2124, 1963.

34. Cavalieri, E.L., Rogan, E.G., Roth, R.W., Saugier, R.K., and Hakam, A. The relationship between ionization potential and horseradish peroxidase/hydrogen peroxide catalyzed binding of aromatic hydrocarbons to DNA. Chem.-Biol. Interactions 47: 87, 1983.

35. Rao, K.R. (Ed.) Pentachlorophenol: Chemistry, Pharmacology and Environmental Toxicology, Plenum Press, New York.

36. The Merck Index (1983) Tenth Edition, Merck and Co., Inc., Rahway, NJ.

37. Au, W., Butler, M.A., Bloom, S.E., and Matmey , T.S. Further study of the genetic toxicology of gentian violet. Mutat. Res. 66: 103, 1979.

38. Au, W., Pathak, S., Collie, C.J., and Hsu, T.C. Cytogenic toxicity of gentian violet and crystal violet on mammalian cells in vitro. Mutation Res. 58: 269, 1978.

39. Michaels, G.B. and Lewis, D.L. Microbial transformation rates of azo and triphenylmethane dyes. Environ. Toxicol. Chem. 5: 161, 1986.

40. Cerniglia, C.E. Aromatic hydrocarbons: Metabolism by bacteria, fungi and algae. Reviews in Biochemical Toxicology 3: 321, 1981.

41. Lijinsky, W., Dormsky, I., Mason, G., Ramahi, H.Y., and Safari, T. The chromatographic determination of trace amounts of polynuclear hydrocarbons in petrolatum, mineral oil and coal tar. Anal. Chem. 35: 952, 1963.

42. Rochkind, M.L., Blackburn, J.W., and Sayler, G.S. Microbial decomposition of chlorinated aromatic compounds. EPA/600/2-86/090, U.S. Environmental Protection Agency, Cincinnati, OH, 1986.

43. Lundquist, K. and Kirk, T.K. De novo synthesis and decomposition of veratryl alcohol by a lignin-degrading basidiomycete. Photochemistry 17: 1676, 1978.

44. Huynh, V.-B., Chang, H.-m, Joyce, T.W., and Kirk, T.K. Dechlorination of chloro-organics by a white rot fungus. T.A.P.P.I. J. 66: 9, 1985.

DETOXIFICATION OF CONTAMINATED SLUDGES USING COMBINED MICROBIOLOGICAL AND PHOTOLYTIC DEGRADATIVE APPROACHES

by: Ralph J. Portier, Kuniko Fujisaki, and Charles B. Henry
Institute For Environmental Studies, Louisiana State University
Baton Rouge, La. 70803

ABSTRACT

Dioxins have long been recognized as major carcinogenic substances associated with creosote and pentachlorophenol contaminated sludges and soils. These hazardous waste materials have posed a significant threat not only to groundwater supplies in the southern United States but also have been recognized as a major potential global source of dioxin contamination worldwide via transport mechanisms such as volatization and particulate transport. Research will be presented on the feasibility of biologically degrading pentachlorophenol and creosote sludge materials using a contact reactor method incorporating the use of acclimated biomass in a highly aerated stirred-tank reactor system. To date, data indicate that significant biotransformation of these listed materials is possible at a loading rate of 20% solids. Significant concern remains with regard to the residual dioxin components associated with this reactor technology. Preliminary laboratory data will also be presented which indicate the possibility of photolytic decomposition occurring as a primary degradative pathway for OCDD and related dioxin contaminants associated with pentachlorophenol biotransformation in these reactors.A secondary pathway involves the use of selected bacterial and fungal strains which appear to further facilitate mineralization. The fate of OCDF and related furan contaminants also found in these wastes will also be discussed.

INTRODUCTION

Dioxins have long been recognized as major carcinogenic substances associated with creosote and pentachlorophenol contaminated sludges and soils. These hazardous waste materials have posed a significant threat not only to groundwater supplies in the southern United States but also have been recognized as a major potential global source of dioxin contamination worldwide via transport mechanisms such as volatization and particulate transport. The Institute for Environmental Studies has for the past four years been involved in extensive research on the feasibility of biologically degrading pentachlorophenol and creosote sludge materials using a contact reactor method incorporating the use of acclimated biomass in a highly aerated stirred-tank reactor system. These sludge materials, referred to as K001 materials, is listed in 40CFR Part 261, Appendix VIII.

Preliminary data from a biological closure of an RCRA site in Tennessee indicated the possibility of photolytic decomposition occurring as a primary degradative pathway associated with pentachlorophenol biotransformation. The objective of our investigation is to evaluate the contribution of photolytic decomposition of dioxins in liquid/ solid contact reactors as a consequence of irradiation, % solids, transport and acclimated biomass introduction. Data will be presented on roughing cell experiments wherein the soils/sludges are suspended and introduced to acclimated biomass.

MATERIALS AND METHODS

SAMPLING PROCEDURES.

Samples for analysis, both water and sludge residuals, were properly identified, labelled and recorded in the lab notebook immediately after collection. All samples were collected, preserved, and transported following the provisions of EPA/SW -846.

LIQUID/SOLIDS CONTACT REACTORS.

Chlorinated dioxins and furans are known to exist in many sludges, contaminated soils, and contaminated slurries of materials having significant hydrocarbon content. Of particular concern to State and Federal agencies are the dioxins and furans found in chloroaliphatic wastes such as creosote waste materials, particularly those materials containing high concentrations of pentachlorophenol (PCP) (14). Liquid /solids contact (LSC) reactors, as shown in Figure 1, were constructed and placed in an environmentally closed laminar flow hood and inoculated with acclimated microbial populations developed in earlier pentachlorophenol studies (12). Specific measurements included microbial ATP for the determination of microbial biomass(13), parent compound disappearance, contribution of incident UV light on photolytic decomposition processes, and post-treatment residual determinations of dioxins using GC/MS. Particular emphasis was on following the degradative pathway of octachlorodibenzo p-dioxin (OCDD) and other dioxin constituents associated with pentachlorophenol and creosote sludges.

Each unit consisted of a 1,000 ml reaction vessel in which toxicants or substrates were introduced via peristaltic pump. Temperature was maintained by a heat lamp system regulated by a proportional indicating temperature controller. pH/ Eh of the reaction vessel was maintained by a series of controllers connected to the peristaltic pumps or gas regulators. Samples were withdrawn aseptically from the reaction vessel by means of micropipet or syringe. Samples consisted of aqueous slurries, grab-sampled from reactor vessels, at periodic intervals. Contents of the agitated reactors were presumed to be homogeneous suspensions. However, all calculations of toxicant residuals were determined on a dry weight basis.

PHOTOLYSIS OF DIOXIN ISOMERS.

Artificial UV light (10 µW/ 300-315nm) was applied to laboratory reactors for 8 h/day at 28°C. UV light penetration into the glass reactors was determined prior to waste loading. Control experiments consisted of tests in which the reactors were not exposed to any incident sunlight or UV source. An illumination level meter was used to determine light exposure. UV intensity readings were determined using a long wave intensity meter.

LIQUID SOLIDS CONTACT STUDIES: PENTACHLOROPHENOL - CONTAMINATED WASH WATERS.

A series of replicate experiments were conducted evaluating both photolytic and photolytic/microbiological methods for biotransformation of pentachlorophenol and its trace chlorinated dioxin/furan contaminants. Abiotic control LSC reactors, containing filter-steriled (0.22µ filter, Nucleopore™) pentachlorophenol contaminated waters under filtered aeration (0.45µ. Nucleopore™) , were agitated in the presence and/or absence of ultraviolet light. Experimental reactors were established with all process parameters and, in addition, inoculated with a Pseudomonas species isolated in previous investigations(12) . This strain had capabilities of biotransforming pentachlorophenol. Both the control and experimental LSC reactors were maintained at 28°C., agitation was constant at 1200rpm over a 21 day treatment period. Biotic control reactors did not receive UV irradiation. GC/MS analyses were determined over the 21 day period for both pentachlorophenol parent compound disappearance as well as the fate of the OCDD residuals associated with this waste. At the conclusion of the experiment, fugitive emission traps and residual biomass were also evaluated for the presence of both pentachlorophenol and OCDD residuals(see GC/MS methods).

LSC CREOSOTE STUDIES STEP #1 ROUGHING CELL REACTOR TESTS.

At the conclusion of initial abiotic and biotic tests on pentachlorophenol wash waters, pentachlorophenol contaminated creosote waste was suspended in LSC reactors over a seven day period. This seven day roughing step provided indications of mixing phenomena for creosote predominantly K001 constituents, and also provided indications of fate of OCDD congeners associated with these wastes. After seven days of high energy contact, the supernatant was transferred to a polishing biological reactor cell where additional biological treatment was again performed for a seven day period(see Figure 1). Over these time frames, GC /MS determinations were made of the primary K001 constituents as well as the chlorinated dioxin and chlorinated furan contaminants.

CORRELATIVE MICROBIOLOGICAL APPROACHES.

To identify microbial contributions to dioxin degradation, two approaches were considered. Sterile L/S contact tests were conducted using the aforementioned laboratory approach. Antibiotics were used to hinder microbial growth and kinetic response. Comparisons were made between abiotic and biotic tests for OCDD removal.

MICROBIAL DENSITY

The Standard Plate Count Method (SPC) is a direct quantitative measurement of the viable aerobic and facultative anaerobic microflora. Four general groups of microorganisms, i.e., bacteria, actinomycetes, yeasts and filamentous fungi were enumerated using colony forming units (CFU) and SPC. Replicate 1.0-ml aliquots were inoculated on Jensen's agar medium (2) supplemented with 40 µg/ml with cycloheximide (Sigma) , to inhibit growth of filamentous fungi. Filamentous fungi and yeasts were enumerated on Martin's agar medium (3), with 30 µg/ml streptomycin (Sigma) and 30µl/ml chlortetracycline (Sigma) to retard bacterial growth. All plates were then incubated for four days at 30°C. Bacteria and actinomycetes were counted on a Biotran III Automatic Colony Counter (New Brunswick Scientific). Yeasts and fungi were enumerated manually.

ADENOSINE 5' TRIPHOSPHATE (ATP)

A modification of the adenosine 5' triphosphate (ATP) assay as advanced by Holm-Hansen and Booth (4), and further presented by Van de Werf and Verstraete (5) and Karl (6), was used for determination of microbial biomass. 1.0 g aliquots from all mesocosms (wet weight) were transferred into dilution bottles containing 99 ml sterile distilled and deionized water and homogenized on a homogenizer (Janke &Kunkel Ultra Turrax SD 45) for about 45 s. A 100 µl aliquot of that suspension was then transferred to a 3 ml plastic vial. The vial was inserted into a Lumac 3M Biocounter (Biocounter M2010, Lumac Systems, USA) and 100 µl of buffer and 100 µl NRB reagent (Nucleotide releasing agent for bacterial cells) was added. ATP was released from microbial cells by adding NRB to a 100 µl sample. After application of this reagent, ATP was measured using the following reactions:

$$\text{luciferin} + \text{luciferase} + \text{ATP} \xrightarrow{Mg^{++}} (\text{luciferin} * \text{luciferase} * \text{AMP}) + pp_i$$

$$(\text{luciferin} * \text{luciferase} * \text{AMP}) \xrightarrow{O_2} \text{decarboxyluciferin} + \text{luciferase} + CO_2 + \text{AMP} + \text{light}$$

Following the injection of 100 µl of a luciferin-luciferase solution (Lumit, Lumac systems) into the vial, light outputs expressed as relative light units (RLU) were determined over a 10 s integration period. Relative light units were expressed as µg ATP/g dry net weight using standardized 10 µl aliquots of a known ATP standard. Quench corrections for each environmental sample were established with 100 µl aliquots of ATP standard /buffer added in place of the 100 µl buffer addition (internal standard method).

RECEIPT AND STORAGE OF SAMPLES.

Samples were transferred from their source to the analytical laboratory accompanied by an "in house" chain of custody form. Since the samples never leave the department, the form functions as a management tool to help schedule work in the laboratory. Samples are stored at 5^0C until extracted.

SAMPLE PREPARATION.

The samples, each approximately 20 ml subsampled into scintillation vials from the experimental reactor vessel or other apparatus, were allowed to clarify into water and sediment/sludge fractions.The two fractions were analyzed separately. The following volume and weight determinations were made: total volume, water fraction volume, wet weight sediment/sludge, dry weight sediment/sludge.

SEDIMENT/SLUDGE EXTRACTION METHOD.

After the water was decanted and wet weight determinations made, the samples were spiked with the following internal (surrogate) standards: 10 µg d-10 acenaphthene, 10 µg d-12 perylene, and 25 ug hexamethylbenzene. The samples were oven dried at 40^0C for 3-6 hours. At this point the sample vial was again weighed for dry weight determination. Approximately 1 g of sodium sulfate was added to ensure complete drying and to aid in extraction efficiency. 15 mls of Dichloro Methane (DCM) was added and extracted with the aid of bath sonication for 12 min. The final extraction volume of 15 ml was subsampled and fractionated on silica-gel columns.

The subsampled extract, typically 250 µl, was reduced to 100 µl for fractionation. The samples were fractionated on activated silica-gel columns into two fractions: a slightly polar fraction eluted off the column with 3.5 mls DCM and a polar fraction eluted off the the column with 3.5 mls methanol. The fractions are labeled F-2 and F-3 respectively. The fractions were then reduced to a final volume of 100 ul and were ready for GC/MS analysis.

Water Fraction Extraction Method.

The water fraction was extracted by a slightly modified EPA method 625: only acid/neutrals were extracted. In addition to the internal surrogate standards listed in the above section, pentafluorophenol was added to verify recovery of the acid fraction, in particular pentachlorophenol.

GAS CHROMATOGRAPHY / MASS SPECTROSCOPY ANALYSIS.

The following is the standard methodology developed for the GC/MS analysis of polynuclear aromatic hydrocarbons (PAHs), heptachlorodibenzofurans (HpCDF), octachlorodibenzofurans (OCDF), heptachlorodibenzodioxins (HpCDD), and octachlorodibenzodioxin (OCDD) in complex sample matrices: i.e., sludge/water samples which have undergone partial microbial decomposition.(Note: High levels of microbial activity and biomass can cause interferences not normally encountered with typical creosote sludge samples.)

Qualitative and quantitative gas chromatography/mass spectrometry (GC/MS) analysis was performed on a Hewlett Packard 5890 GC equipped with a 12 meter Ultra-2 capillary column (0.2 MM ID; 0.33μ film thickness) directly interfaced to a Hewlett Packard 5970B mass spectrometer. The F-2 fraction was analyzed twice. First in the scanning mode and then by selected ion monitoring (SIM) for detection and quantitation of the the PCDDs and PCDFs.

SCAN Method.

When operating in the scanning mode the oven was held at 50^{0}C for 3 min then increased to 260^{0}C at a rate of 8^{0}C/min and held for 8 min. The mass spectrometer was scanned between 45-500 amu at a rate of approximately 1 scan/sec. The electron multiplier voltage (EMV) was set 200 volts above the tuning value. The inlet system was operated in the splitless mode with the purge off until 30 seconds into the analysis. The column flow is 0.68 ml/min at 100^{0}C.

SIM Method.

When operating in the SIM mode the GC was initially at 100^{0}C for 3 min and increased to 260^{0}C at 20^{0}C/min. until 180^{0}C where the rate is changed to 6^{0}C/min until the final temperature of 260^{0}C was reached then held for 10 min. Detailed information about the characteristic ions used and their time windows is given in the Table 1.

Table 1: SIM Method Characteristic Ions.

WINDOW	RT	ION	COMPOUND	ADDITIONAL INFORMATION	
1	5.8	147	HMB	M -- CH_3	S
	6.1	164	d-10 acenaphthalene	M	S
	15.0	322	1,2,3,4-TCDD	M+2	Q
	15.0	320	1,2,3,4-TCDD	M	C
	16.3	430	OCBP	M+4	Q
	16.3	432	OCBP	M+6	C
2	21.6	264	d-12 perylene	M	S
		408	HpCDF	M+2	C
		410	HpCDF	M+4	Q
		424	HpCDD	M+2	C
		426	HeptCDD	M+4	Q
3	26.2	458	OCDD	M+2	C
	26.2	460	OCDD	M+4	Q
	26.2	442	OCDF	M+2	C
	26.2	444	OCDF	M+4	Q

S	surrogate standard
Q	quantitation ion
C	confirmation ion

Analytes of interest were quantitated by an internal standard method calibrated by a 5-point external standard curve. Daily, or during each 8 hr analysis period, a single concentration of the mixed standard was analyzed to verify the validity of the calibration curve. If the daily standard differed by greater than 20 %, a new standard curve was made.

RESULTS AND DISCUSSION

Biotransformation Of Pentachlorophenol-Contaminated Surface Water.

As shown in Figure 2, pentachlorophenol contaminated waters were biologically reacted over a time frame of 21 days. Control and three experimental contact reactors were monitored for residual pentachlorophenol concentration expressed in parts per billion (ppb). As determined by GC/MS analyses, reactors had initial concentrations of 3,000-4,000 ppb PCP . Experimental reactor #1 had an initial concentration of .5,222 ppb. After three days of biological contact, all experimental reactors, #1, #2 and #3, indicated significant reductions in total PCP. After seven days of continuous contact, concentrations of PCP approached < 10ppb. At the conclusion of the study at 21 days, residual concentrations were again < 10ppb. However, the control reactor showed some fluctuations in PCP over time but remained rather consistent in terms of minimal reduction and total concentration.

Figure 2 shows the same experiment in which liquid chromatography (HPLC) analyses were performed. Again, concentrations were approximately the same at time . Experimental reactors were significantly reduced in concentrations over the first seven days with minimal residual levels noted for days 14 and 21. Control reactors showed minimal, if any, losses in PCP concentration. PCP residuals noted at day 21 reflected concentration variables due to evaporative loss of water from the reactors, i.e., a concentrating factor.

GC/MS SIM determinations of OCDD residuals in control and experimental contact reactors for the pentachlorophenol contaminated water are shown in Figure 3. The initial concentrations of OCDD ranged from 3.4 ppb to 13.9ppb for all LSC reactors tested. After three days of biological contact, both control and experimental bioreactors showed significant reductions in OCDD concentrations. The most significant removal rate of OCDD occurred in experimental reactors where significant biological activity was taking place. The photolytic control reactors, however, also showed significant reductions in OCDD concentrations. This reflects perhaps the contribution of ultra violet radiation exposing suspended water droplets in the reactor during high energy mixing. Abiotic control reactors without UV showed no loss in total OCDD concentrations.

Subsequent analysis of volatiles traps of all experimental and control reactors show no volatilization and no volatile loss of OCDD or related dioxin congeners from the reactor within limits of detection. Again, GC/MS detection limits for OCDD are 1.0ppb. Subsequent follow-up studies with higher concentrations of pentachlorophenol have also shown the similar relationships for OCDD removal and abiotic photolytic decomposition experiments where only ultra violet light was illuminating the pentachlorophenol contaminated wash waters. A more complete presentation of these data will be presented in a subsequent manuscript. An evaluation of filtered biomass from these reactors did not show detectable OCDD residuals.

Biotransformation Of Creosote Waste K001 Constituents.

Figures 4 and 5 provide information on the residual levels of key K001 constituents for all reactors for roughing cell phase one biological treatment. The roughing step involves the actual resuspension and solubilization of creosote and pentachlorophenol materials over a seven day period.

This key initial step forces the solubilization of the K001 constituents as a result of the addition of surfactant (Triton X100, Sigma) and pH adjustment (to 7.3) resulting in the increased availability of these materials for biological attack.

The data presented show high concentrations of fluorene, phenanthrene and fluoranthrene for initial waste loading. Reactor cell #1 had the highest levels of these K001 constituents in concentrations exceeding 7,000 ppm. Reactors cells #2 - #4 had concentrations approaching 8,000 ppm or less with the exception of phenanthrene, averaging 15,000 ppm. It is important to note that the initial concentrations varied in terms of chemical content, however, they all represented a 20% loading rate based on solids for all reactors. With combined microbial addition and surfactant addition, the residual level for fluorene, phenanthrene, fluoranthrene and pyrene were greatly reduced after seven days of continuous aeration and agitation.

Residual concentrations from this roughing cell step, which would normally be transferred to a polishing reactor step , averaged in concentration between 500 and 4,000 ppm with phenanthrene appearing to be the most resistant to the continuous agitation over a seven day treatment period. In reactor test #3, minimal microbial levels were noted as determined by direct plate counts and microbial ATP estimates. As a consequence of this, minimal removal levels for all K001 constituents were noted. In particular, pyrene and crysene resulted in negligible biodegradation. Phenanthrene was Marginally reduced from 13,000 ppm to approximately 10,000 ppm. Fluoranthrene and fluorene appeared to be the most significantly reduced of the K001 constituents.

Reactor #1, having the highest K001 constituents loading rates, had the greatest reduction in total hydrocarbon content. In particular, pyrene and crysene were more dramatically reduced in reactor cell #1 as compared to reactor cell #3. High biomass levels were noted in reactor cell #1. Microbial ATP levels exceeded 10^9 cells per ml for continuous treatment.

Discussion.

Optimal mixing of creosote waste materials can result in significant reductions in K001 constituents. Reactor cell #3 had minimal performance in K001 reductions. This correlated with poor microbial performance and mixing. Thus, a key component in the ability to biologically transform these materials rests with the ability to sufficiently mix and suspend by wet weight the creosote materials in question. In subsequent investigations not reported here, more optimal mixing of the K001 materials was achieved with a reconfiguration of the reactor cell. This reactor cell includes baffle systems to prevent settling and incomplete mixing. Rates of K001 disappearance responded to this improvement in reactor design.

Biotransformation of Polynuclear Aromatics.

Figures 6 and 7 provide information on the initial and final concentrations of key five-ring polynuclear aromatics found in creosote/ pentachlorophenol waste materials. Of particular interest is the benzofluoranthrene and benzo-(a) pyrene constituents of these wastes. As in the previous data sets on K001 constituents, reactors #1, #2 and #4 provided significant reduction in the five ring polynuclear aromatics. Reactor cell #1 , having the highest accumulated biomass, indicated the greatest reductions to < 500 ppm for all constituents. Reactor cell #3 which experienced incomplete mixing showed negligible reduction in the benzo-(a) pyrene. Note in particular that benzo-(b) fluoranthrene was not reduced during this 7 day mixing step.

Biotransformation of Chlorinated Dioxins/Dibenzofurans.

Figures 8 and 9 show initial and final concentrations of chlorinated dioxins in all reactor cells. Reactor cell #3, which suffered incomplete mixing due to the heavy oil and grease content, nevertheless gave indications of reduction in OCDD. However, the Hp CDD concentrations were only marginally reduced from about 8.2 ppm to 5.6 ppm. In reactor cells # 1, #2 and #4, again the HpCDD concentrations were also only marginally reduced on the average of 15% - 20%.

However, the OCDD concentrations were removed at much higher levels. These reductions ranged from 25% to 45% for a 7 day biotreatment period.

Similar phenomena were noted for the chlorinated dibenzofurans (see Figures 10 and 11) HpCDF concentrations varied in overall treatment efficiency. In reactor cell #3, the HpCDF concentrations increased from 2.2 ppm to over 3.4 ppm. OCDF concentrations, however, varied depending upon reactor initial concentration and the contact period. The greatest improvement in OCDF removal occurred in reactors #2 and #4 with trace quantities detected in both instances.

CONCLUSIONS

The focus of these preliminary investigations has been to evaluate the consequences of mixing and microbiological addition to creosote/ pentachlorophenol waste materials during the initial steps of liquid/solid contact technology. Data indicate that changes are, indeed, occurring in terms of the total quantity of all primary K001 constituents involved. However, the five ring polynuclear aromatics are marginally reduced. Mixing performance plays an important role in terms of the total residual materials over a seven day mixing period.

Figure 12 provides a composite summary of this initial treatment step for liquid/solids contact reactor processing. For the chlorinated dioxins and chlorinated dibenzo furans. HpCDD and HpCDF concentrations were not as significantly reduced in the initial seven day treatment period. However, OCDD and OCDF concentrations were dramatically reduced. At this time, it is difficult to determine the primary contributor to the OCDD and OCDF removal rates. High biomass concentrations were realized in reactor cells #1, #2 and #4. However, reactor cell #3 had only marginal biomass growth. Nevertheless, the OCDD levels of removal in reactor cell #3 were comparable to the other three reactors in terms of total reduction rates. Abiotic control reactors showed essentially no reduction in K001 constituents.

The investigations are incomplete at this writing with regard to the actual contributions of ultra violet light in the reactor process. Pure culture studies have been completed where ultra violet light was the primary mechanism for degradation of the prime chlorinated dioxin/furan constituents. Experiments on the contributions of the incident ultra violet light in polishing reactor cells (Step 2) will be completed shortly.

Nevertheless, it can be stated that significant biological activity is achievable for creosote/pentachlorophenol waste in the reactor configurations as outlined. Biomass concentrations reflected incomplete mixing and also reflected high oil and grease loading rates. Analysis of volatiles exported from the reactor cells by mixing and air sparging did not contain dioxin or furan congeners. Comparisons of biotic reactor cells to abiotic reactor cells showed reductions in volume and specific toxicants, notably PNAs, occurred only in biotic reactors.

As reported by Crosby, 1983, the reduction of TCDD, a dioxin congener associated with Agent Orange herbicide formulations, is rapid and complete within a matter of hours for UV light. All dioxins absorb light above 295 nm, so sunlight can serve as a light source. However, three criteria must be met for dioxin photolysis to be practical: the wave lengths of incident light must correspond to appreciable absorption by TCDD/HpCDD/OCDD, the light must penetrate the medium to contact the dioxin component, and a source of extractable hydrocarbons must be present (although water is not very effective, formulating solvents and related hydrocarbon materials, i.e., K001 constituents would suffice) (Crosby and Wong, 1977). The roughing cell reactors provided situations in which these criteria have been met.

Finally, a recent paper by Pereira, 1986, suggests that in the presence of elevated concentrations of dioxins and furans, particularly OCDD and HpCDD, microbial attack may be indicated under aerobic conditions. Specific variations in congener profiles over time indicated that specific microorganisms may be participating in primary or secondary degradative mechanisms for dioxin removal in chlorinated hydrocarbon sludges. Data generated to date in our investigations tend to support these observations.

ACKNOWLEDGEMENTS

The research presented in this manuscript was supported by funding from the Hazardous Waste Research Center, Louisiana State University, Baton Rouge, La. (Cooperative Agreement CR 813888, ORD/EPA)

LITERATURE CITED

[1] Bossert, I., Kachel,W.M. and Bartha, R. Applied and Environmental Microbiology, April 1984. pp. 763-767.

[2] Jensen, H.Z., Soil Science, Vol. 30, 1930, pp. 59-77

[3] Martin, J.P.,Soil Science, Vol. 69, 1950, pp. 215-233.

[4] Holm,-Hansen, O. and Booth, C.R. Limnology and Oceanography, Vol. 11, 1966, pp. 510-519.

[5] Van de Werf, R. and Verstraete, W. in Proceedings, International Symposium Analytical Applications of Bioluminescence and Chemiluminescence, Schram et al. Eds., 1979., pp. 333-338.

[6] Karl, D.M., Microbiology Reviews, Vol. 44, 1980, pp. 739-796.

[7] EPA/530-SW-84-015 Dec. 1984. Permit Guidance Manual on Hazardous Waste Land Treatment Demonstrations.

[8] Federal Register/ Vol. 49 No. 209. Oct. 1984/ Rules and Regulations, Method 610, pp.533-541.

[9] Alexander, M. in Microbial Degradation of Pollutants in Marine Environments, A.W. Bourquin and P.H. Pritchard, Eds., EPA-600/9-79-012.

[10] Portier, R.J. and Meyers, S.P., Developments in Industrial Microbiology, Vol. 22,1982, pp. 459-478.

[11] Portier, R.J., Chen, H.M. and Meyers, S.P. Developments in Industrial Microbiology, Vol. 24, 1983, pp. 409-424.

[12] Portier, R.J. and Meyers, S.P. in Toxicity Screening Procedures Using Bacterial Systems, Liu, D. and Dutka, B., Eds., Marcel Dekker, Inc., New York, 1984, pp. 345-379.

[13] Portier, R.J. in Validation and Predictability of Laboratory Methods for Assessing the Fate and Effects of Contaminants in Aquatic Ecosystems, ASTM STP 865, T.P. Boyle, Ed., American Society for Testing and Materials, Philadelphia, 1985, pp. 14-30.

[14] Crosby, D.G. and Wong, A.S. 1977. Environmental degradation of 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD). Science 195:1337-1338.

[15] Pereira, W.E., Rostad, C.E., and Sisak, M.E. 1985. Geochemical investigations of polychlorinated dibenzo-p-dioxins in the subsurface environment at an abandoned wood-treatment facility. Environ. Toxicol. Chem. 4:629-639.

[16] Crosby, D.G. 1978. Conquering the monster: The photochemical destruction of chlorinated dioxins. ACS Symposium Ser. 73:1-12.

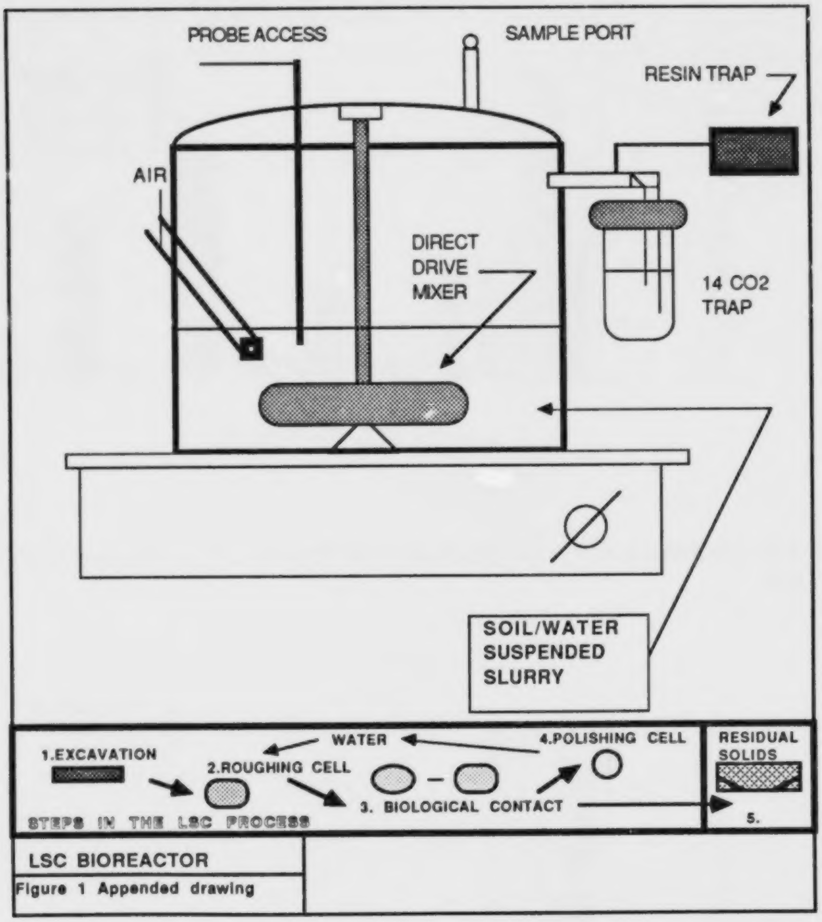

PROBE ACCESS
SAMPLE PORT
RESIN TRAP
AIR
DIRECT DRIVE MIXER
14 CO2 TRAP
SOIL/WATER SUSPENDED SLURRY
1.EXCAVATION
WATER
2.ROUGHING CELL
4.POLISHING CELL
RESIDUAL SOLIDS
3. BIOLOGICAL CONTACT
5.
STEPS IN THE LSC PROCESS
LSC BIOREACTOR
Figure 1 Appended drawing

Figure 1. General Design and Process Flow Diagram of LSC Reactor Approaches

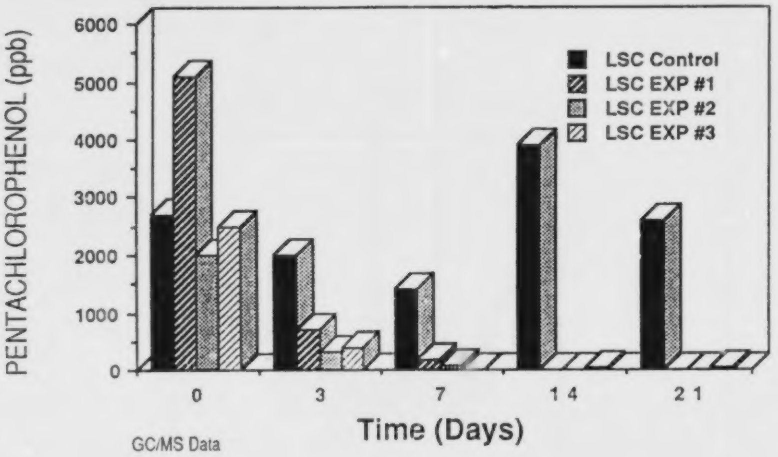


Figure 2. Gas Chromatography Biotransformation Profiles Of Pentachlorophenol-Contaminated Wastewaters

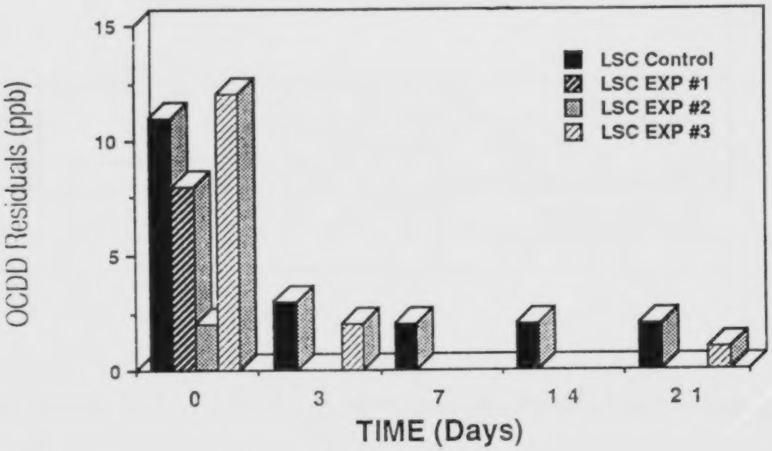


Figure 3. Chlorinated Dioxin Residuals Of Biologically- Treated Pentachlorophenol Wastewaters

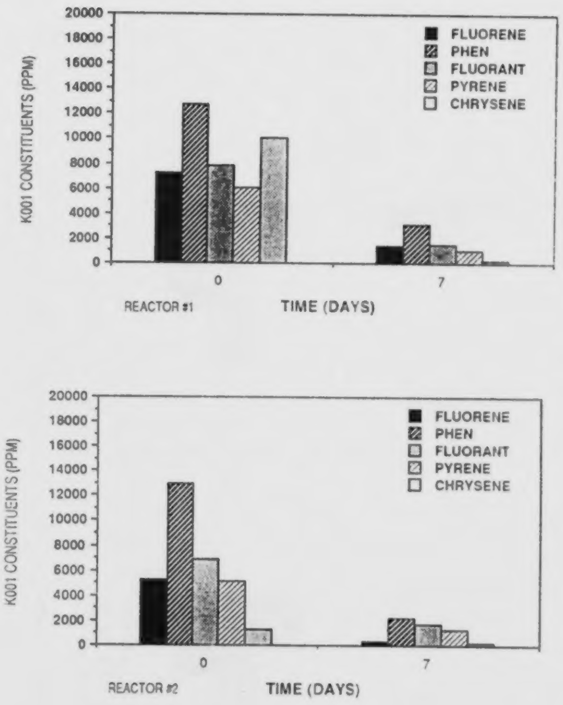


Figure 4. K001 Waste Residuals: Roughing Cell Tests

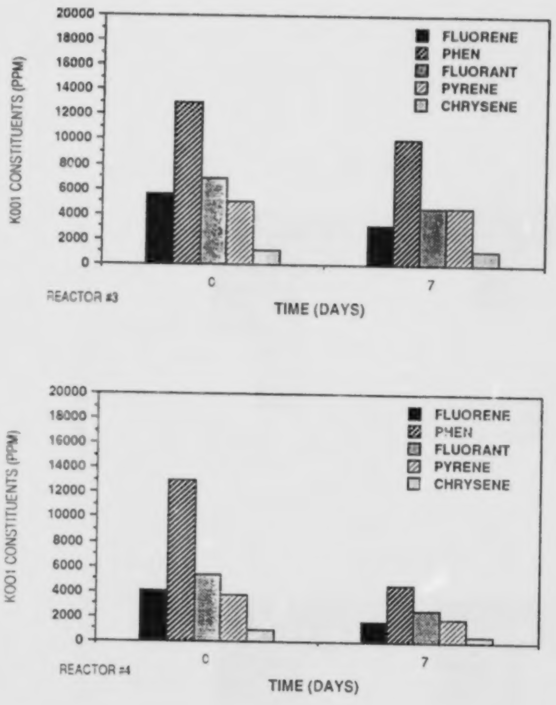
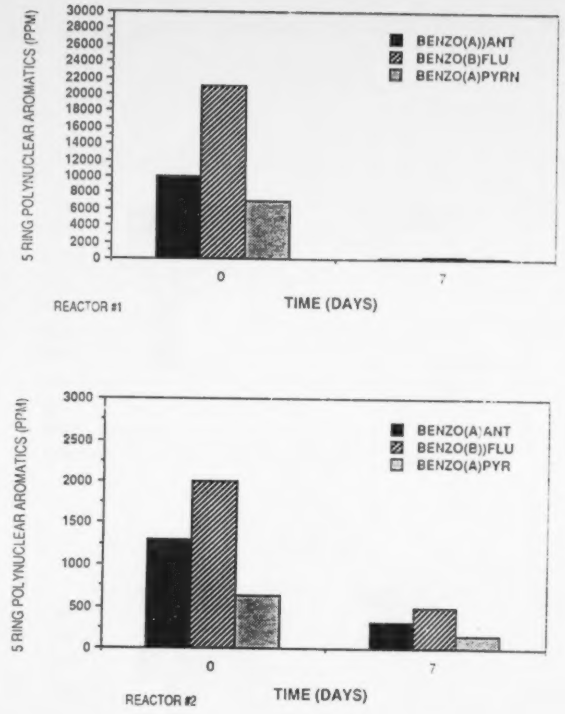


Figure 5. K001 Waste Residuals: Roughing Cell Tests



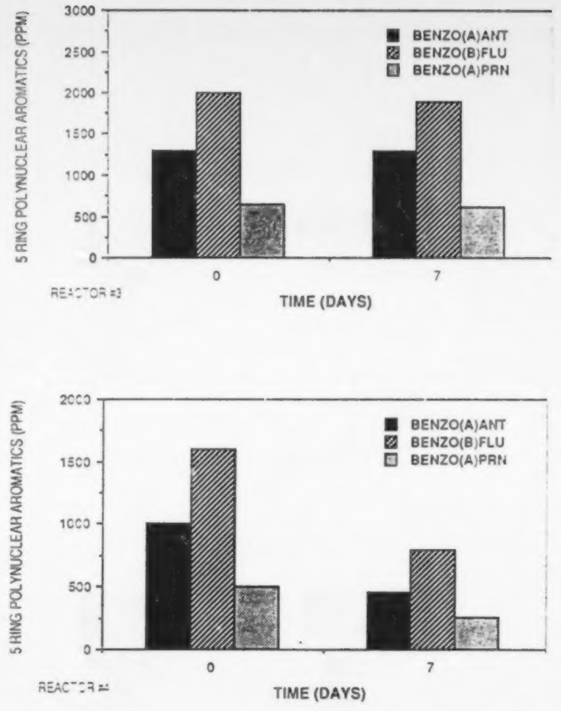


Figure 6.

Figure 7.

Polynuclear Aromatic Hydrocarbon Residuals: Roughing Cell Tests

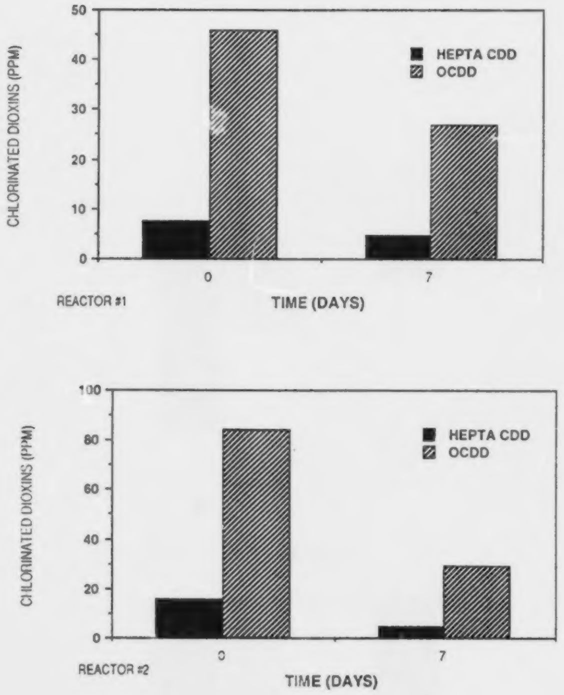


Figure 8.

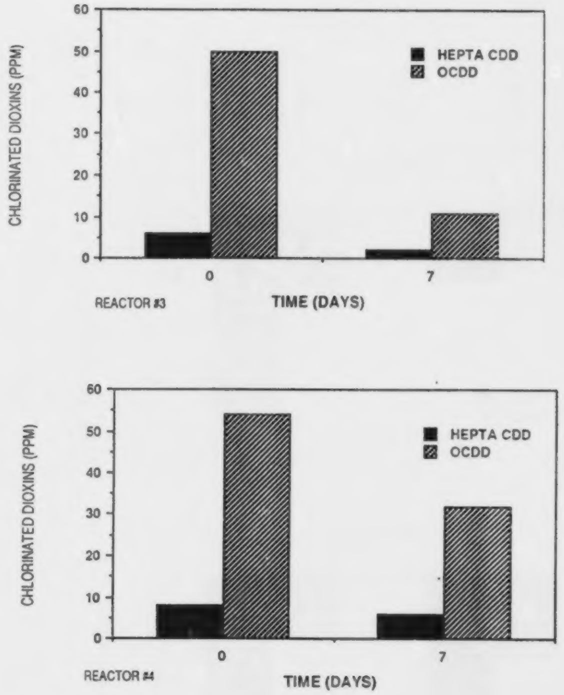


Figure 9.

Chlorinated Dioxin Profiles Of Contact Reactor Roughing Cells

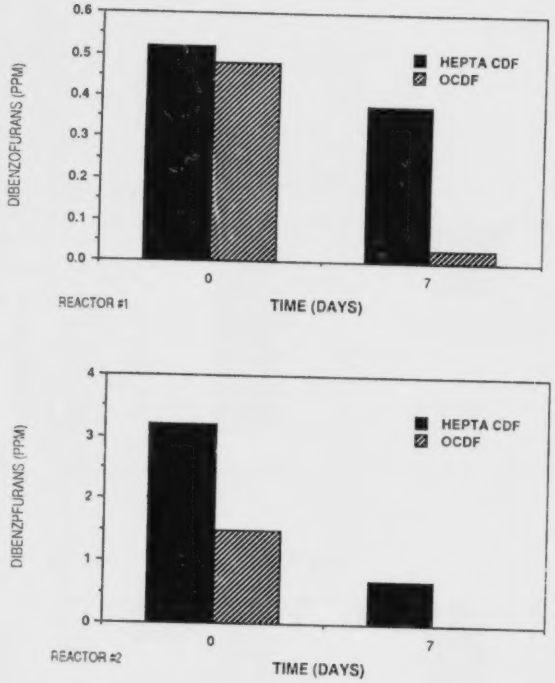


Figure 10.

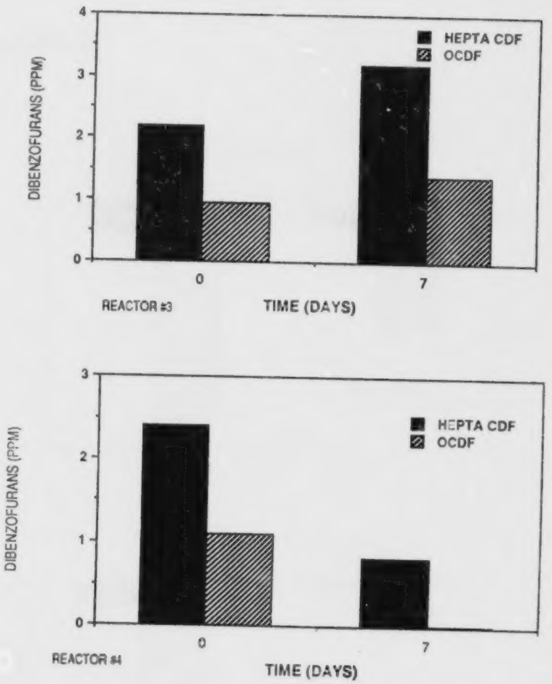
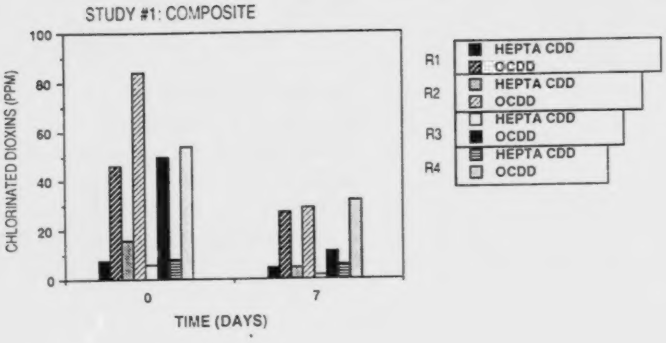


Figure 11

. Chlorinated Furan Profiles Of Contact Reactor Roughing Cells



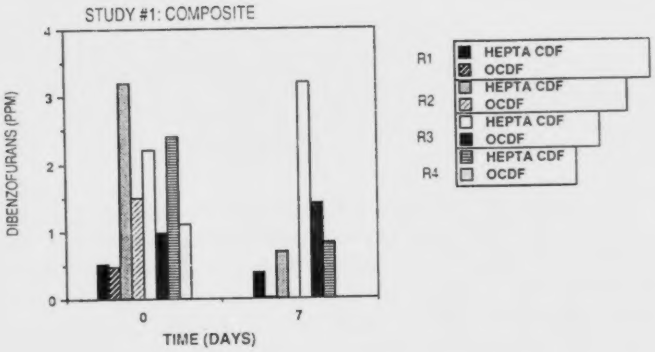


Figure 12. Composite Of Chlorinated Furan/Dioxin Residuals In Roughing Cell Experiments

TESTING OF TREATMENT SYSTEMS FOR CYANIDE BEARING HAZARDOUS WASTES

by: Douglas W. Grosse
HWERL, U.S. EPA
Cincinnati, OH 45268

Sardar Q. Hassan
Michael P. Vitello
Margaret K. Koczwara
Dept. of Civil & Environmental Engineering
University of Cincinnati
Cincinnati, OH 45221-49TE

ABSTRACT

As a part of the program to perform hazardous waste treatment technology assessments, the U.S. EPA has been directed to evaluate technologies applicable to the treatment of metal and cyanide bearing wastes. Bench- and pilot-scale studies have been conducted on spent process electroplating wastes (RCRA Code F007) at U.S. EPA's Test and Evaluation Facility. A series of unit processes have been evaluated: alkaline chlorination, precipitation, filtration, resin adsorption and activated carbon. Several different treatment trains have been evaluated for the purpose of determining the optimum treatment.

INTRODUCTION

Alkaline chlorination is a treatment technology which has shown to be successful in destroying free cyanides from aqueous metal/cyanide waste resulting from cyanide electroplating operations. However, complexed (non-amenable) cyanides are often left untreated and may pass into precipitation processes which generate metal hydroxide/cyanide sludges or are discharged as final effluents. It is desirable to destroy all the cyanide rather than to have it mixed with metal hydroxide sludges which, in most cases, are land disposed. Further treatment may be required to remove the residual cyanides. The objective of this study is to evaluate the most effective way to remove (destroy) hazardous components from aqueous metal/cyanide waste streams using conventional alkaline chlorination in conjunction with additional polishing or removal steps. These additional technologies are anionic exchange and precipitation of ferrocyanide complexes in the form of ferri-ferrocyanide (Prussian Blue). Metals treatment consisted of lime precipitation and cationic exchange.

APPROACH

This study was conducted in conjunction with the University of Cincinnati (UC) at the U.S. EPA's Test and Evaluation (T&E) Facility, in Cincinnati, Ohio. Results from bench- and pilot-scale research were used to evaluate the treatment of an electroplating cyanide spent process stream (RCRA Code F007). Configurations (treatment trains) of unit processes were evaluated based upon the ability to optimize treatment. Performance was evaluated at selected design parameters, e.g., ORP, pH, dosage and retention times. It is hoped that data generated by this study will benefit commercial manufacturing operations utilizing on-site waste treatment systems, off-site treatment storage and disposal facilities (TSDFs) and regulatory agencies (federal, state and local) in understanding the parameters which influence treatment of cyanide bearing electroplating wastes.

Initially, bench-scale studies were conducted for the purpose of optimizing unit process parameters. Then, a conventional pilot system was installed to test the operation of the various unit processes employed. Lastly, treatment technology modifications were evaluated at bench-scale to meet the following treatment objectives:

- Highest quality final effluent devoid of metal and/or cyanide constituents, and
- Least amount of cyanide present in the metal hydroxide sludges.

Results are presented from each phase of study.

WASTE DESCRIPTION

In order to perform this work it was necessary to obtain the appropriate permits (TSDF and RD&D permits) to legally import an electroplating process waste (synthesized F007). This waste is defined as a "spent cyanide plating bath solution from electroplating operations (except for precious metals electroplating spent cyanide plating bath solutions)." (1) The source of the wastewater for the experiments described in this paper was a local Cincinnati metal finisher who has been involved in joint EPA-industry demonstration projects in the past. The metal finishing plant is a multi-process facility which incorporates zinc, brass, chromium, tin, bright nickel and cadmium plating. Twelve 55-gallon drums of synthesized F007 electroplating waste were acquired. Drag-out from plating operations was added to give specific concentrations of cyanide and heavy metals. Results from the characterization of this waste are provided in Table 1.

TABLE 1. CHARACTERIZATION DATA FOR THE RAW WASTE

Pollutant	Symbol	Concentrations (mg/L)
Cyanide (total)	CN(T)	418-462
Cyanide (not amenable to chlorination)	CN(NA)	3-10
Sulfide	S	0.70-0.90
Fluoride	F	1.80-2.10
Arsenic	As	0.02-0.03
Barium	Ba	0.04
Cadmium	Cd	24.8-26.2
Chromium (total)	Cr	0.06-0.12
Copper	Cu	52.5-58.5
Nickel	Ni	11.9-12.8
Silver	Ag	0.01
Zinc	Zn	11.2-11.9
Methylene chloride		0.01
Chloroform		0.02
Bis-(2-ethylhexyl)phthalate		0.02
TOC		315
TSS		44.7

The raw waste was analyzed for cyanide, inorganics and organics in order to determine applicable treatment options.

The rationale behind the waste selection was based upon obtaining a raw waste that would challenge the efficiency of the conventional alkaline chlorination/precipitation treatment process. A profile for an initial wastestream was developed taking into consideration waste characteristics, permit limitations and safety. In order to achieve our objectives, a prescribed composition of both cyanide (amenable and non-amenable) and heavy metals was required. It was determined that a synthesized wastestream was preferable. Although the selected wastestream would be atypical of those wastestreams generated by electroplating job-shops, it may be more representative of mixed aqueous metal/cyanide wastestreams that would be treated at off-site commercial treatment, storage and disposal facilities (TSDF). Future studies will examine different waste matrices and constituent concentrations.

TREATMENT TECHNOLOGY EVALUATIONS

The assessment of bench- and pilot-scale treatment of the subject waste was based upon (1) bench-scale process optimization studies; (2) monitoring of significant process parameters during pilot-scale operation; and (3) evaluation of treatment technology modifications. In total, five treatment trains were evaluated as having potential for the treatment of the characterized waste. All sampling and analyses were performed in accordance to standard procedures as described in the EPA's Office of Solid Waste Manual (2). Metal analysis was performed on an Inductively Coupled Plasma (ICP) spectrometer while organics were analyzed on a gas chromatograph/mass spectrometer (GC/MS). For bench-scale testing alkaline chlorination and lime precipitation were performed in a batch mode while ion-exchange operations were performed in a continuous mode by use of laboratory burettes. All sludges and solids were settled and filtered prior to ion exchange to avoid fouling and clogging of the resins. Upon decanting of the supernatant, the residual sludge slurry was filtered. The resulting filter cake was analyzed for cyanide and metals concentrations.

OPTIMIZATION OF UNIT PROCESS PARAMETERS

As a result of the raw waste analysis (Table 1) an initial conventional treatment strategy was identified as having potential for treatment of the characterized waste. This treatment train included two-stage alkaline chlorination for cyanide destruction, lime precipitation for metals removal, sulfide precipitation, multi-media filtration, cation exchange and carbon adsorption for organics removal. Figure 1 shows a schematic of this initial treatment configuration.

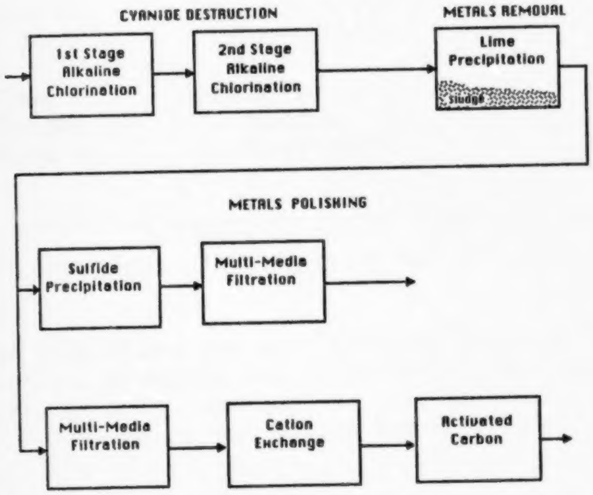

CYANIDE DESTRUCTION
METALS REMOVAL
1st Stage Alkaline Chlorination
2nd Stage Alkaline Chlorination
Lime Precipitation
Sludge
METALS POLISHING
Sulfide Precipitation
Multi-Media Filtration
Multi-Media Filtration
Cation Exchange
Activated Carbon

Figure 1. Treatment train A - conventional treatment train for cyanide and metal bearing waste.

The bench unit process optimization studies determined optimum conditions for two-stage alkaline chlorination (dose, retention time and pH), lime and sulfide precipitation (dose jar tests at selected pH values) and polyelectrolytic addition (dose, pH, turbidity and conductivity). Breakthrough conditions were determined for filtration (TSS), ion-exchange (metals) and carbon adsorption (TOC). Results of these studies are shown in Table 2.

TABLE 2. OPTIMUM UNIT PROCESS PARAMETERS

First Stage Alkaline Chlorination:	pH	11.5
	ORP	300 mV
	Residence time	60 min.
Second Stage Alkaline Chlorination:	pH	8.5
	ORP	750 mV
	Residence time	60 min.
**Lime Precipitation:	pH	10.5
	Residence time	15 min.
**Sulfide Precipitation	pH	10.5
	Residence time	15 min.
	Dose	333 mg/L
Flocculation:	Residence time	15 min.
	Polyelectrolyte type	cationic
	Polyelectrolyte dose	20 mg/L
*Clarification:	Residence time	30 min.
	Loading rate	0.104 gpm/ft^2
*Cation Exchange for Metals Polishing:	Loading rate	1 gpm/ft^3
	Resin type	Amberlite IRC-718
	Resin capacity	1 meq/ml. wet resin

*Supplemented from literature and vendor information.
**The flocculation and settling for these precipitation processes is the same.

Upon analysis of the data gathered from the preliminary bench tests, it was determined that sulfide precipitation and carbon adsorption offered little improvement in the treatment of this wastestream. As a result, these two unit processes were omitted from the preliminary pilot test.

PILOT SCALE TESTING

Based upon the results generated from bench-scale optimization of unit processes, a pilot-scale treatment train (Figure 1) was prepared for operation. The system incorporated four unit processes: alkaline chlorination, lime precipitation (incorporating coagulation, flocculation and settling), multi-media filtration and cationic exchange. The pilot system was designed for a flow rate of 1 gpm, however, due to waste quantity limitations, the flow rate in the alkaline chlorination process was reduced to 0.5 gpm. A complete pilot run was conducted in two days; with 2-stage alkaline chlorination performed on the first day and metals treatment on the following day.

Sampling was performed allowing for unit process hydraulic retention times. For example, the effluent sample collected following two-stage alkaline chlorination was taken two hours (the residence time for 2-stage alkaline chlorination) after the corresponding influent sample. Detailed QA/QC was adhered to which included the collection of field duplicates and spikes. Data resulting from this run is presented in Table 3.

TABLE 3. CYANIDE & METALS ANALYSES FOR PILOT TESTING

Sample Source	Concentration (mg/L) CN (T)	CN (NA)	Cd	Cr(T)	Cu	Ni	V	Zn	TOC	TSS
Raw waste	365	25.0	29.3	0.04	93.7	14.6	0.01	13.1	315	44.7
Alk. chl.	17	11.8	29.6	0.04	66.0	14.5	0.02	12.7	241	459*
Lime prec.	21	14.5	0.7	0.06	2.1	0.8	ND	0.3	165	31.7
Cation exch.	18.7	17.2	0.01	0.07	0.02	0.2	ND	ND		

* This increase in TSS can be attributed to solids generated during the alkaline chlorination step.
CN(T) is total cyanide.
CN(NA) is cyanide not amenable to chlorination.
Cr(T) is total chromium.

Although metals concentrations were significantly reduced following cation exchange (<.2 mg/L) total cyanide was still passing through the final effluent in concentrations exceeding the local allowable discharge limit of 10 mg/L (at 18.7 mg/L). Upon further analyses of the treated waste, iron (Fe) concentrations in the raw waste (13 mg/L) and final effluent (7 mg/L) suggested that the 18.7 mg/L cyanide in the final effluent was complexed with the Fe in the form of ferrocyanide ($Fe(CN)_6^{4-}$). An additional polishing step would be required to remove the remaining cyanide complex. In order to better understand the treatment of this waste, a series of alternative treatment trains were investigated in bench studies.

In observing the values of the cyanide concentrations (both total and non-amenable), there is a noticeable degree of variability. This may be attributed to matrix effects (interferences), variation of waste composition from drum to drum (although the synthesized waste was pre-mixed in a single process tank prior to separation into drums) and problems encountered with the development of analytical methods. This variability is more prevalent with the non-amenable analysis than with the total cyanide analysis. This phenomenon was documented by the quality control (QC) and quality assurance (QA) data reported for the pilot-scale testing, which is as follows:

Non-amenable

Precision (RPD):	52.5% (±45.3%)
Spike Recovery:	68.0% (±20.0%)
Standard Recovery:	71.0% (±17.7%)

Total Cyanide

Precision (RPD):	29.6% (±23.3%)
Spike Recovery:	80.0% (±22.6%)
Standard Recovery:	75.6% (±11.5%)

EVALUATION OF TREATMENT TECHNOLOGY MODIFICATIONS

Based upon the results of the pilot run, four additional treatment trains (B, C, D, & E) were developed to effect treatment technology modifications in order to achieve lower cyanide concentrations in the final effluent and the lowest amount of cyanide settling out in the hydroxide sludge. These treatment trains included all or some of the following unit processes: alkaline chlorination, lime precipitation, anion exchange for complexed cyanide removal, cationic exchange for metals removal and precipitation of ferrocyanide complexes in the formation of Prussian Blue. These units were operated in a manner which simulates the pilot-scale operating conditions listed in Table 2. For cyanide polishing Amberlite IRA-958 was selected at a loading rate of 1 gpm/ft^3. Capacity of the resin is 1.2 - 2.3 lbs CN/ft^3. Results of applying these modified treatment trains to the synthesized F007 waste are presented below.

A schematic of Treatment Train B is shown in Figure 2. This treatment train evaluates the effectiveness of cation exchange resin in removing metals from the raw waste and segregating metals from sludges produced during alkaline chlorination. Alkaline chlorination and anion exchange follow the initial cation exchange metal removal step. Sludges produced during this step are settled and the supernatant filtered before anion exchange. Performance of this treatment train is shown in Table 4. Cation exchange in Treatment Train B failed to remove all the metals (Cu - 63.2 mg/L; Ni - 11.1 mg/L) and the majority of these unadsorbed metals precipitated in the alkaline chlorination sludge (as is illustrated in Table 4). Initially, it was presumed that the cationic exchange resin was not contacting properly with the waste. As a result, a separate stirred beaker test was performed maximizing the contact of the waste with the cation resin. However, similar results were obtained refuting our initial presumption. It is quite possible that Cu and

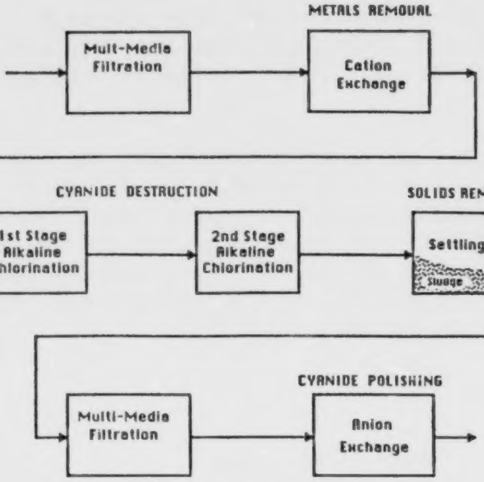

METALS REMOVAL
Multi-Media Filtration
Cation Exchange
CYANIDE DESTRUCTION
1st Stage Alkaline Chlorination
2nd Stage Alkaline Chlorination
SOLIDS REMOVAL
Settling
Sludge
CYANIDE POLISHING
Multi-Media Filtration
Anion Exchange

Figure 2. Treatment train B - metals removal by cation exchange prior to alkaline chlorination.

Ni were complexed with the cyanide prior to alkaline chlorination, thus, inhibiting ion exchange removal. The succeeding alkaline chlorination step then broke the Cu and Ni cyanide complexes precipitating the two metals in the following clarification step. The effluent from this clarifier showed a substantial reduction in Cu (1.36 mg/L) and Ni (1.45 mg/L) concentrations. Effluent from the anion exchange column contained 26 mg/L of total cyanide.

TABLE 4. CYANIDE AND METALS ANALYSES FOR TREATMENT TRAIN B

	Concentrations (mg/L)									
Sample Source	CN (T)	CN (NA)	Cd	Cr(T)	Cu	Ni	V	Zn	Ag	Fe
Raw waste	179	31.5	25.2	0.04	58.5	11.4	0.00	10.3	0.04	5.49
Cation exchange	288	30.5	0.58	0.01	63.2	11.1	0.00	0.17	0.05	2.99
Alk. chl.	22.0	**	0.89	0.02	61.1	11.3	0.00	0.22	0.06	4.92
Clarifier	29.0	26.0	0.28	0.02	1.36	1.45	0.00	0.03	0.04	6.48
Anion exchange	26.0									

**CN(NA) was determined to be greater than CN(T); actual number is not available.

Treatment Train C converts free cyanide into a ferrocyanide complex ($Fe(CN)_6^{4-}$) for subsequent removal by an anion exchange resin (IRA-958). Then, lime precipitation and cation exchange are employed for metal removal and polishing, respectively. A schematic of this treatment train in shown in Figure 3.

The objective of this treatment strategy was to completely remove the cyanide prior to lime precipitation so that cyanide would be prevented from accumulating in the hydroxide sludge. Conversion of free cyanide into the ferrocyanide complex was achieved by dosing with ferrous sulfate ($FeSO_4$) at a pH of 8.5. Excess ferrous sulfate forms ferrous hydroxide precipitate ($Fe(OH)_2$) which was settled and filtered prior to anion exchange. Results of this treatment train are presented in Table 5.

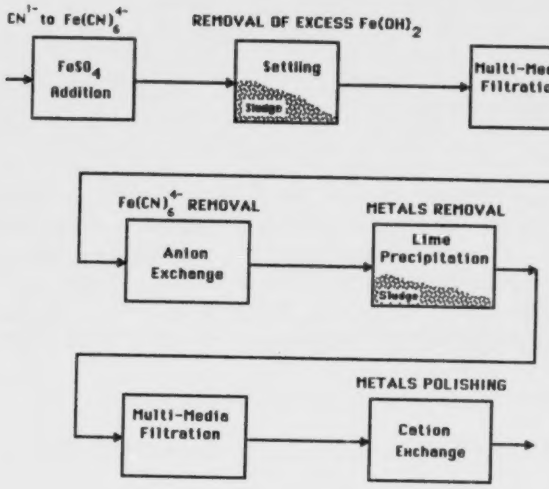

CN^{1-} to $Fe(CN)_6^{4-}$
REMOVAL OF EXCESS $Fe(OH)_2$
$FeSO_4$ Addition
Settling
Sludge
Multi-Media Filtration
$Fe(CN)_6^{4-}$ REMOVAL
Anion Exchange
METALS REMOVAL
Lime Precipitation
Sludge
Multi-Media Filtration
METALS POLISHING
Cation Exchange

Figure 3. Treatment train C - initial removal of all cyanide in the form of a ferrocyanide complex using anion exchange.

In Treatment Train C, again the anion exchange resin failed to remove all the cyanide (25 mg/L CN in the effluent), part of which then precipitated with the hydroxide sludge. The $Fe(OH)_2$ sludge contained 9310 mg CN/kg wet sludge 48.1 mg Cd/kg wet sludge, 38.7 mg Cr/kg wet sludge, 68.7 mg Ni/kg wet sludge and 1800 mg Zn/kg wet sludge. With the accumulation of metals and cyanide in the hydroxide sludge this treatment option proved to be deficient in achieving desirable residuals separation of cyanide and metals.

TABLE 5. CYANIDE AND METALS ANALYSES FOR TREATMENT TRAIN C

Sample Source	CN (T)	CN (NA)	Cd	Cr(T)	Cu	Ni	V	Zn	Ag	Fe
	Concentrations (mg/L)									
Raw waste	350	33.0	29.5	0.04	68.7	14.8	0.01	12.2	0.07	13.3
Anion exchange	25.0	**	1.41	0.00	0.30	0.00	0.00	0.05	0.04	0.50
Lime prec.	12.0	**	1.49	0.01	0.32	0.07	0.01	0.05	0.06	0.65
	mg/kg wet sludge									
$Fe(OH)_2$ sludge	9310	**	48.1	38.7	8.70	68.7	6.90	1800	4.40	38500

**CN(NA) was determined to be greater than CN(T); actual numbers are not available.

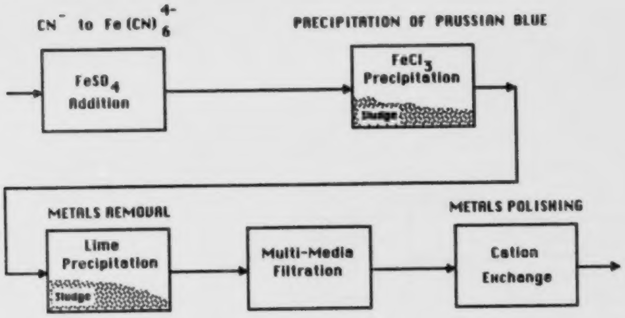

CN^- to $Fe(CN)_6^{4-}$
PRECIPITATION OF PRUSSIAN BLUE
$FeSO_4$ Addition
$FeCl_3$ Precipitation
Sludge
METALS REMOUAL
Lime Precipitation
Sludge
Multi-Media Filtration
METALS POLISHING
Cation Exchange

Figure 4. Treatment train D - initial removal of cyanide in the form of Prussian Blue.

Figure 4 shows a schematic of Treatment Train D. The purpose of this option was to initially convert all free cyanide into the ferrocyanide complex, with subsequent precipitation in the form of Prussian Blue, ($Fe_4[Fe(CN)_6]_3$). Ferrous sulfate and ferric chloride ($FeCl_3$) are used in the two reactions at pH values of 8.5 and 6.5, respectively. Lime precipitation and cation exchange follow as metal removal processes. Table 6 exhibits the results generated from running this option. In Treatment Train D, the Prussian Blue precipitation step failed to remove all the cyanide (83 mg/L CN in effluent). Furthermore, the sludge concentrations were (mg/kg wet sludge) 1690 for Cd, 42.5 for Cr, 53 for Cu, 106 for Ni and 567 for Zn in addition to the 15,600 for CN and 62,600 for Fe.

TABLE 6. CYANIDE AND METALS ANALYSES FOR TREATMENT TRAIN D

Sample Source	Concentrations (mg/L)									
	CN (T)	CN (NA)	Cd	Cr(T)	Cu	Ni	V	Zn	Ag	Fe
Raw waste	350	33.0	29.5	0.04	68.7	14.8	0.01	12.2	0.07	13.3
Pr. Blue prec.	83.0	73.0	0.44	0.00	55.8	13.6	0.01	0.15	0.04	1.93
Lime prec.	83.0	72.5	0.70	0.04	58.7	11.6	0.05	0.17	0.09	1.49
	(mg/kg wet sludge)									
Pr. Blue sludge	15600	15500	1690	42.5	53.0	106	1.50	567	4.10	62600

In Treatment Train E, as shown in Figure 5, a conventional treatment train for cyanide bearing metal plating waste (similar to Figure 1) has been augmented with polishing for complex cyanide and metals using ion exchange columns. Anion exchange is employed for the polishing of cyanide, (particularly the stable ferrocyanide complexes), while cation exchange was used for metal polishing. As Table 7 shows, this treatment train achieved significant reduction of constituent metals and cyanide concentrations in the effluent, with total cyanide and metal concentrations at or below 1 mg/L.

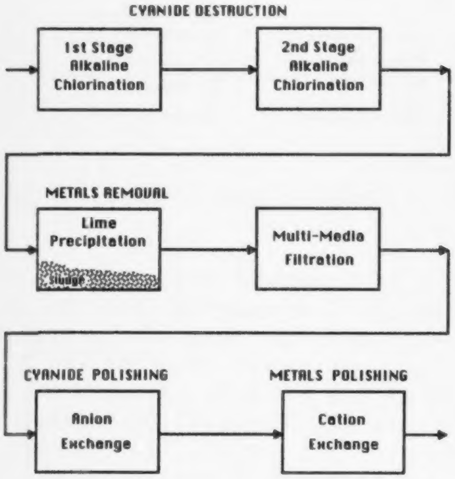

CYANIDE DESTRUCTION
1st Stage Alkaline Chlorination
2nd Stage Alkaline Chlorination
METALS REMOVAL
Lime Precipitation
Sludge
Multi-Media Filtration
CYANIDE POLISHING
METALS POLISHING
Anion Exchange
Cation Exchange

Figure 5. Treatment train E - cyanide polishing with anion exchange resins after lime precipitation.

TABLE 7. CYANIDE AND METALS ANALYSES FOR TREATMENT TRAIN E

	Concentrations (mg/L)									
Sample Source	CN (T)	CN (NA)	Cd	Cr(T)	Cu	Ni	V	Zn	Ag	Fe
Raw waste	513	30.0	25.3	0.06	55.8	11.9	0.01	10.4	0.02	3.72
Alk. chl.	36.0	21.5	24.6	0.06	57.8	11.9	0.00	10.6	0.06	4.62
Lime prec.	30.0	23.5	0.48	0.05	1.08	0.32	0.03	0.24	0.05	8.69
Anion exchange	0.10	0.00	0.07	0.04	0.14	0.07	0.02	0.05	0.04	0.09
Cation exchange	0.15	0.00	0.05	0.05	*1.04	0.07	0.01	0.05	0.02	0.03
	(mg/kg wet sludge)									
Lime prec. slud.	2530	878	8410	3.70	22400	4270	4.00	3610	12.7	275

* This increase is due to copper screening being used as an underdrain for the bench-scale cation exchange columns.

DISCUSSION

After analyzing the treatment data generated from the four treatment trains (B, C, D, & E) it was concluded that Treatment Train E provided the best treatment for this particular waste. Although unsuccessful in completely separating CN^- from the metals in the hydroxide sludge (2530 mg/kg wet sludge CN^-), Treatment Train E exhibited the lowest CN^- concentration in the effluent (0.15 mg/L). Metals concentrations in the cationic exchange effluent were below sewage discharge limits (POTW).

Future work will confirm the results of these bench studies on treatment technology modifications. Again, the pilot treatment system will be modified to run on the optimum treatment train (E). Results of these studies will be presented as soon as they become available. Other studies are also in progress to determine how the cyanide-bearing sludge formed by Treatment Train E can be further treated to reduce its CN^- content prior to land disposal.

CONCLUSIONS

1. Although alkaline chlorination was unable to lower the total cyanide below 17 mg/L in the synthetic F007 waste studied, anionic exchange polishing reduced the total cyanide concentration to less than 1 mg/L.

2. Lime precipitation were able to reduce metal concentrations in the waste to local discharge limits, but with polishing (multi-media filtration, anion and cation exchange) metals concentrations were lowered to <0.1 mg/L for each metal except copper.

3. A complete separation of cyanide and metals in residual sludges was not achieved by using the unit processes studied in this research.

REFERENCES

1. Code of Federal Regulations 40, Part 261, revised as of July 1987.

2. U.S. EPA, Office of Solid Waste, "Test Methods for Evaluating Solid Wastes" SW-846, 3rd Edition, November 1986.

FIELD EXPERIENCE WITH THE KPEG REAGENT

by: Alfred Kornel
Charles J. Rogers
Harold Sparks
Hazardous Waste Engineering Research Laboratory
U. S. Environmental Protection Agency
Cincinnati, Ohio 45268

ABSTRACT

Chemical reagents prepared from polyethylene glycols and potassium hydroxide (KPEGs) have been demonstrated under mild conditions (25° - 140°C) to dehalogenate PCBs, PCDDs, and PCDFs with laboratory destruction efficiencies exceeding 99.9999%. The reaction mechanism is nucleophilic substitution at an aromatic carbon.

Bench scale studies have already established conditions for PCB destruction to less than 1 ppm and for PCDDs and PCDFs to less than 1 ppb. Toxicological tests have established that arylpolyglycol by-products from KPEG reactions are non-toxic. The non-toxic property of the by-products may allow for delisting and on-site disposal of treated materials. In July and August 1986, a 2700 gallon KPEG reactor was used in Butte, Montana, on a wood preserving site and in Kent, Washington, on a waste disposal site to successfully detoxify PCDDs and PCDFs (120 ppb - 200 ppm) in 17,000 gallons of liquid waste to non-detectable levels. A reactor designed to treat both liquids and solids has been tested on selected Superfund and Department of Defense sites. These field studies have validated conditions for destruction of PCBs, PCDDs, and PCDFs to acceptable levels required by the regulations. This presentation will review treatment data, regulations for treated materials, costs, and the potentials of KPEG for the destruction of a variety of halogenated pollutants.

INTRODUCTION

Chlorinated dibenzo-p-dioxins (PCDDs), polychlorinated biphenyls (PCBs), and chlorinated dibenzofurans (PCDFs) are three series of related compounds that gained notoriety for their high toxicity and persistence in the environment. In the last few years PCDDs and PCDFs have increasingly been identified in chemical product waste streams as well as in effluents from incineration processes.

Most of our knowledge of PCDDs and PCBs as environmental contaminants is associated with their occurrence in soils, sediments, combustion particulates, and in fish. In most cases, this contamination stems from improper waste disposal of highly toxic PCDDs in such products as hexachlorophene or 2,4,5-trichlorophenoxy acid herbicides (2,4,5-T, herbicide orange). The occurrence of PCDDs in fish is considered to be the major source of these compounds in humans. While PCDDs arise principally from dimerization of chlorophenols, PCDFs are primarily produced from pyrolysis of PCBs.

Although the toxicological profiles with aquatic organisms are limited, it has been determined that short-term exposure of fish to low ppb and ppt of PCB and PCDD concentrations respectively, cause decreased growth rate, poor survival and increased mortality. PCDDs, however, are considered to be a probable human carcinogen.

The accumulation of PCDDs, PCBs, and other toxic halogenated compounds in the environment and living systems is a serious problem that has been well documented. Although a great amount of work has been done by many groups on the area of direct chemical decomposition of halogenated organics, relatively little effort has been directed toward on-site chemical detoxification.

The "cleanup" of a contaminated site, which often appears in the news media, is not really a permanent detoxification but rather a transfer of a toxic spill from one region to another. As an example, PCB-contaminated soil along some of the highways of North Carolina has been dug up, and has only been removed, at great expense, to another area of that state and landfilled. These PCBs are still in the environment and will persist there until they are removed and destroyed.

The chemical stability of PCDDs, PCBs, and other haloorganics precludes their destruction by conventional refuse incineration methods. Most municipal incinerators cannot achieve the high temperatures necessary to destroy these chemicals in refuse. The surprisingly high volatilization rates of PCBs and other chlorinated aromatic compounds raises questions over the use of land disposal for these materials.

Currently, some commercial chemical methods are available to chemically alter or destroy PCBs and other haloorganics in contaminated oils. The chemical methods developed by Acurex, Goodyear, and Sun Ohio involved dispersion of metallic sodium in oil or the use of sodium-biphenyl or naphthalene mixtures. Because of the reactivity of sodium with water, some of these reagents cannot be used efficiently to directly decompose PCDDs or PCBs in soils, sludges, sediments and dredgings. Other chemical reactions have been evaluated for dehalogenation of environmental pollutants but have not been found to be adaptable to field conditions (1,2,3,).

Biological treatment of PCDDs, PCBs, and other hazardous pollutants is also receiving attention. The efficacy of microbes to destroy toxic halogenated compounds has not been fully evaluated by U.S. EPA or independent laboratories.

KPEG PROCESS

During the summer of 1978 a new chemical reagent was synthesized and used to effectively dechlorinate PCB-contaminated oils (4). Since that time a series of reagents has been prepared from potassium hydroxide and polyethylene glycol (KPEGs) which, with heating, produce rapid dehalogenation of haloorganic compounds (5,6,7,8).

In the KPEG reagent preparation, potassium hydroxide reacts with polyethyene glycol (molecular weight approximately = 400) to form an alkoxide (see Equation 1). The alkoxide in turn reacts initially with one or more of the chlorine atoms on the aryl ring to produce an ether and potassium chloride salt (see Equation 2). In some KPEG reagent formulations, dimethylsulfoxide (DMSO) is added as a cosolvent to enhance reaction rate kinetics by improving rates of extraction of aryl halide wastes into the alkoxide phase (6).

$$\text{HO PEG} + \text{KOH} \dashrightarrow \text{KO PEG} + H_2O \qquad (1)$$

$$\text{Aryl-Cl} + \text{KO PEG} \dashrightarrow \text{Aryl -O- PEG} + \text{KCl} \qquad (2)$$

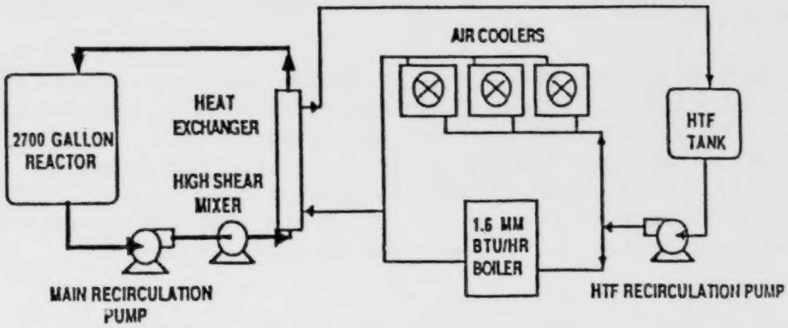
In 1982, detailed investigations were initiated to determine the effects of variable reaction parameters on the rate and extent of chemical decontamination of soils (9). This research focused almost exclusively on the direct chemical treatment of PCDD-contaminated soil. The first field investigation, initiated in January 1986, was aimed at identifying treatment conditions for chemical destruction of PCDDs and PCDFs in oil stored on a wood preserving site in Butte, Montana (10).

PURPOSE

Research and field investigation studies were initiated in January 1986, to determine if a chemical reagent, prepared from potassium hydroxide and polyethylene glycol, could be used to treat PCDD and PCDF contaminated oil at an industrial wood preserving site near Butte, Montana. The wood preserving site contained approximately 9000 gallons of light petroleum oil collected previously from groundwater over a period of two years. The oil contained 3.5% pentachlorophenol, PCDD and PCDF homologs ranging from 422 ppb of tetra-isomers to 83,923 ppb of octa-isomers. Because of the presence of these highly toxic chlorinated dioxins and furans, the oil could not be transported off-site for incineration. Bringing in and operating a mobile incinerator for on-site destruction of contaminated oil was rejected because of high costs.

In April 1986, U.S. EPA Region 8 agreed, after a review of laboratory data, that the chemical process, based upon a potassium polyethylene glycol (KPEG) reagent, could be used to decontaminate the PCDD/PCDF contaminated oil on-site.

The mobile field equipment employed to implement the previous chemical process comprises of a 2700-gallon batch reactor mounted on a 45-foot trailer equipped with a boiler/cooling system and a laboratory/control room area. Heating of the raw oily waste/APEG reagent mixture was achieved by the recirculation of the oil and reagent through a pump, a high shear mixer, and a tubeheat exchanger which was heated using a boiler or cooled through a series of fin-type air coolers. A schematic is shown below:


AIR COOLERS
HEAT EXCHANGER
2700 GALLON REACTOR
HIGH SHEAR MIXER
HTF TANK
1.6 MM BTU/HR BOILER
MAIN RECIRCULATION PUMP
HTF RECIRCULATION PUMP

The process was employed in July 1986, to successfully destroy PCDDs and PCDFs (1000 ppm) in 9000 gallons of oil waste to non-detectable levels (Table 1).

Table 1. TREATMENT OF CONTAMINATED OIL, BUTTE, MONTANA

Contaminants CDD/CDF	Concentration in Untreated Oil (ppb)	Concentration in Treated Residue (ppb) 70°C, 15 min.	100°C, 30 min.	*MDC
TCDD (2,3,7,8-)	28.2	-	-	0.65
TCDD (total)	422	-	-	0.37
PeCDD	822	-	-	0.71
HxCDD	2982	-	-	2.13
TCDF (2,3,7,8-)	23.1	12.1	-	0.28
TCDF (total)	147	33.3	-	0.35
PeCDF	504	-	-	0.36
HxCDF	3918	4.91	-	0.76
HpCDF	5404	5.84	-	1.06
OCDF	6230	-	-	2.62

---

*Minimum detectable concentration in parts per billion.

In May 1987, the KPEG was used at the request of U.S. EPA Region 7 to destroy TCDD in 20 gallons of 2,4-D/2,4,5-T formulation stored in a 55-gallon drum at an abandoned pesticide formulation facility in Omaha, Nebraska.

On January 22, 1987, documentation was provided to U. S. EPA's Director, Office of Emergency and Remedial Response, recommending the "Establishment of KPEG as the Best Developed Alternative Technology (BDAT) for Four RCRA Hazardous Waste Streams: PCBs and Ethylene Dibromide; Pentachlorophenol-oil and Spent Solvents Contaminated with Dioxins and Furans" (11). This recommendation was approved in 1987 by the Office of Emergency and Remedial Response in its Superfund cleanup efforts. Future efforts are directed at decontamination of soils, sediments, and sludges.

KPEG TREATMENT OF PCB-CONTAMINATED SOIL

In July 1987, a small KPEG reactor was transported to Moreau, New York, at the request of U.S. EPA Region 2, and used successfully to treat approximately 400 lbs. of PCB-contaminated soil.

The purpose of conducting the demonstration at Moreau was two fold: 1) to confirm that the KPEG reaction is effective in a 40 gallon reactor in the dechlorination of PCBs in soil to acceptable levels (< 2 ppm) and to gather data that will be used to design the larger 2 cubic yard reactor which will be jointly tested by U.S. EPA and the U.S. Navy in Guam. The results from the Moreau field tests (Table 2) clearly demonstrated that PCBs in soil ranging from 138 to 7012 ppm can be dechlorinated by KPEG to less than 10 ppm.

In November 1987, a new improved 400 gallon Littleford mixer was purchased, modified as a KPEG reactor, and will be field tested on 30 tons of soil on the U.S. Navy's Public Work Center in Guam. The PCB concentration in this contaminated soil range from 2500-4500 ppm. Field tests with the new reactor will commence on March 28 and will be completed by May 15, 1988.

Soil samples have been received from the Guam site, treated with KPEG and analyzed to establish treatment conditions to lower PCBs to less than 2 ppm. The laboratory testing and analysis for the Guam site follows.

GUAM PCB-CONTAMINATED SOIL TREATMENT AND REAGENT RECOVERY

The APEG treatment of PCB-contaminated soil is a rather straightforward process. It consists essentially of placing the contaminated soil into a reactor followed by a 50% by weight portion of the KPEG reagent. After loading, stirring and heating is commenced. Low speed stirring is required for intimate contact of reagent and contaminated soil. Heating causes two major effects, the first being distillation of water from the reaction mixture and secondly, to increase reaction rates. Typically, the vat temperature of the reactor remains near 105-110°C until the majority of water is distilled off (30-45 minutes) after which the reactor temperature slowly rises to ca 135-150°C. The total time for a typical reaction is from 5-6 hours.

After the required elapsed time, any condensate is removed and extracted for residual PCBs. The flask containing the treated soil/reagent mixture is

TABLE 2. TEST RESULTS FROM MOREAU FIELD DEMONSTRATION OF KPEG PROCESS

Run #1		Run #2		Run #3		Run #4	
Reaction time (hours)	PCB concentration (ppm)	Reaction time (hours)	PCB concentration (ppm)	Reaction time (hours)	PCB concentration (ppm)	Reaction time (hours)	PCB concentration (ppm)
0	138	0	756	0	7012	0	680
1.25	0.22	0.25	50.6	1	228	1	19.7
		4	1.46	3.25	23	3.25	6.5
				6.25	9.6	7	0.91

cooled to 40-50°C and filtered on a Buchner funnel. An additional 25-30 ml of water is slurried with the reactor contents to aid in filtration.

After filtration and partial drying to 10-20% moisture, samples of the treated soil are removed and extracted for PCB (Aroclor) determination.

Recovered reagent/water is saved for reuse on subsequent decontamination runs. In this case recovered reagent from 2-3 runs is pooled, an additional quantity of 60% KOH solution or KOH pellets are added, and the used reagent is added to said reactor containing the contaminated soil. The process is then continued.

PCB ANALYSIS OF TREATED SOIL

The soil coming from the reactor is extracted for residual PCB or Aroclor determination. This process is as follows: 10 gram aliquots of the soil are placed into 125 ml screw-top Erlenmeyer flasks to which is added 30-35 ml of hexane/acetone (1:10), this is placed on a gyrorotary mixer at 120-130 rpm for one hour. The extract is carefully decanted into a 250 ml separatory funnel through a small funnel loosely packed with glass wool. This extraction is repeated twice again using hexane/acetone 1:1 and 10:1. All extracts are combined in said separatory funnel and the extracts are washed three times with 50 ml of water. The washed remaining hexane extract is placed into a KD apparatus fitted with a 10 ml receiver and is concentrated to ca 2-5 ml. The equipment is internally washed with hexane ca 2-4 ml and then the receiver is removed, filled to the 10 cc level and agitated. Approximately 2-3 ml of this sample is removed, placed into a 3.5 ml septa sealed glass sample container, and subjected to gas chromatographic analysis, either to an electron capture detector (EDC) or mass spectrometer (MS).

ANALYTICAL PROCEDURES

Generally, the in-house analytical procedure analyzed for residual Aroclor(s) via capillary GC-ECD. In this system a 30 meter 0.32 mm I.D. DB-5 column, using an SGE cold on-column injector and a electron capture detector with Nitrogen make-up gas is employed for routine PCB analysis. However, for the Guam PCB/KPEG process, a HP GC-MSD with related data system for the analytical work has been utilized. In this case, the GC is equipped with a split/splitless injector set to the splitless mode. The pumping requirements of the MSD require either use of a narrow bore capillary column (0.22 mm I.D.), or a jet seperator for use with packed columns. The narrow bore DB-5 column was used in this work.

The MSD is set to acquire data from M/Z 250-500 over the 16 to 32 minute range. The temperature program used for the GC is 40°C for 5 minutes ramp to 180°C at 25°C per minute, hold 2.5 minutes then ramp to 280°C at 5°C per minute, and hold 10 minutes. The total time per run is approximately 42 minutes. This method permits us to resolve the Aroclor mixture and is reliable for as low as 10 ppm of the Aroclor mixture.

For the analytical requirements to be used for the Guam PCB detoxification utilizing APEG, we have been requested to use the Dry Color Manufacturers

Association (DCMA) PCB mixture. This mixture contains mono-thru-deca chlorobiphenyls. Any residual PCB peaks will be quantitated by comparison to this mixture. For example, were a hexachlorobiphenyl to remain after soil treatment, it would be quantified by comparison to the DCMA hexachlorobiphenyl. The maximum residual PCB levels which are permissible in this work are to be 2 ppm per resolvable PCB component. Therefore, all PCB peaks detected after treatment must be below 2 ppm (as shown in Figures 1,2,3).

CONCLUSION

As shown, the KPEG reagent has demonstrated its capability to reduce PCDDs and PCDFs to non-detectable levels in a variety of matrices. Further, the reagent can be used to reduce PCB levels from the thousands of ppm occurring from Aroclors 1248, 1254, 1260 and 1262 to levels below 2 ppm within a reasonable time frame. This demonstrates the use of KPEG systems applicability to these pollutants in a variety of matricies.

REFERENCES

1. Miller, J. Nucleophilic Aromatic Substitution. Elsevier Press, Amsterdam, 1968.

2. Yoshikazu, K. and Regen, S. L. Poly (ethylene glycols) are Extraordinary Catalysts in Liquid/Liquid Two Phase Dehydrohalogenations. J. Org. Chem. 47, 1982, (12) 2493-2494.

3. Andrews, A., Cremonesi, P., del Buttero, P., Licondra, E. and Malorano, S. Nucleophilic Aromatic Substitution of $Cr(Co)_3$-Complex Dihaloarenes with Thiolates. J. Org. Chem. 1983, 48 3114-3116.

4. Pytlewski, L. L., et al. Method for Decomposition of Halogenated Organic Compounds. U.S. Patent 4,400,552 and 4,337,368.

5. Kornel, A., Rogers, C. J. PCB Destruction: A Novel Dehalogenation Reagent. J. Hazardous Materials. 12 (1986) 161-176.

6. Peterson, R. L. Method For Decontaminating Soil. Patent Number 4,574,013, March 4, 1986.

7. Brunelle, D. J. and Singleton, D. A. Destruction/Removal of Polychlorinated Biphenyls from Non Polar Media Reaction of PCB with Poly (ethylene glycol)/KOH. Chemosphere, 12, (2), 1983, 183-196.

8. Li, and Alper H. Poly (ethylene glycol) Promote Reactions of Vinylic Dibromides. Dehydrohalogenation and Palladium - Catalyzed Formal Oxidative Homologation. J. Org. Chem. 1986, 51, 4353-4356.

9. Rogers, C. J. Chemical Treatment of PCBs in the Environment. EPA-600/9-83-003, 197-201.

10. Peterson, R. Potassium Polyethylene Gycol Treatment of PCDD/PCDF - Contaminated Oil in Butte, Montana. IT Corp./Galson Research Corp., Project #86-706, July 1986. U.S. EPA Contract 68-03-3219.

11. Rogers, C.J., Kornel, A. Chemical Destruction of Halogenated Aliphatic Hydrocarbons. U.S. Patent 4,675,464, June 23, 1987.

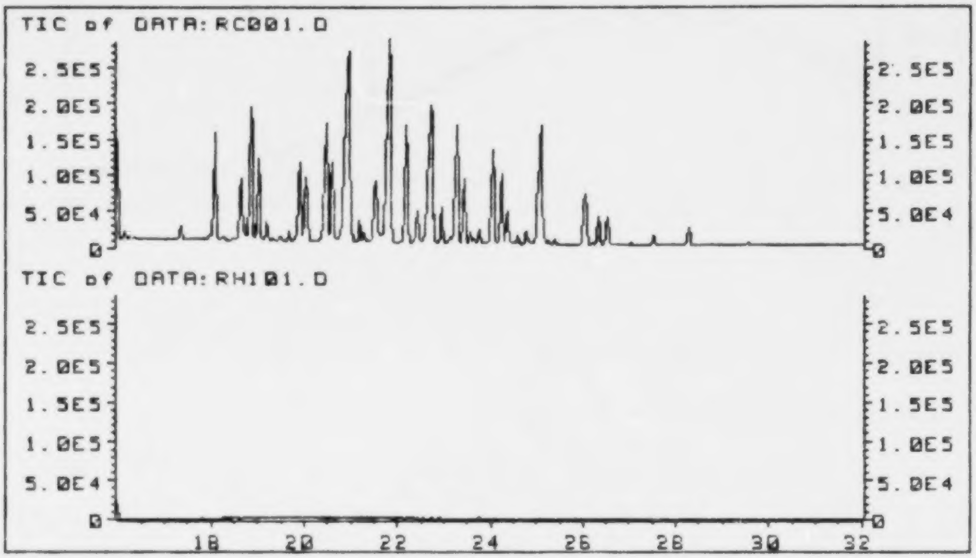


Figure 1

UPPER: Aroclor 1260 extracted from Guam soil.

LOWER: Guam soil after treatment.

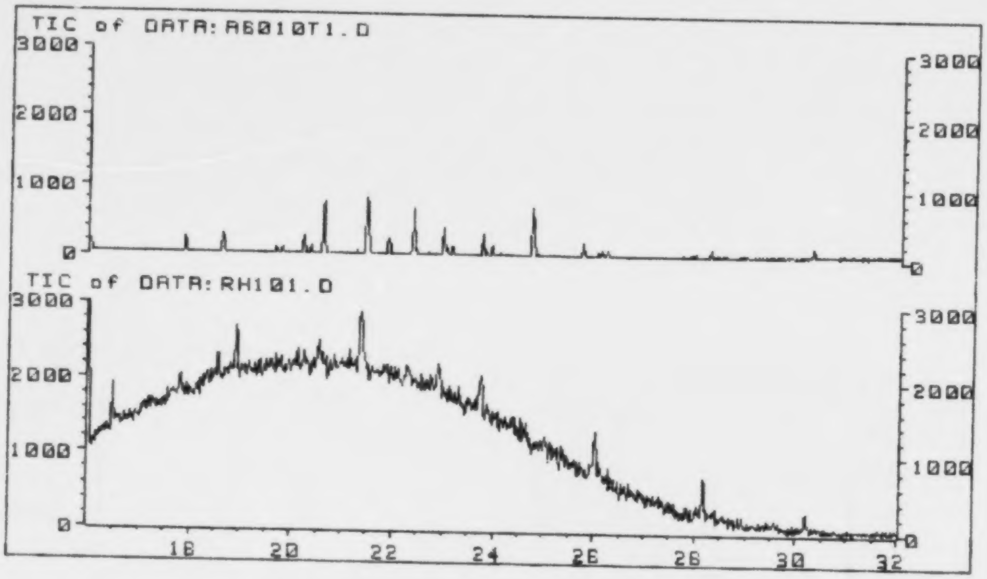


Figure 2

UPPER: Aroclor 1260 at 10 ppm.

LOWER: Guam soil after treatment.

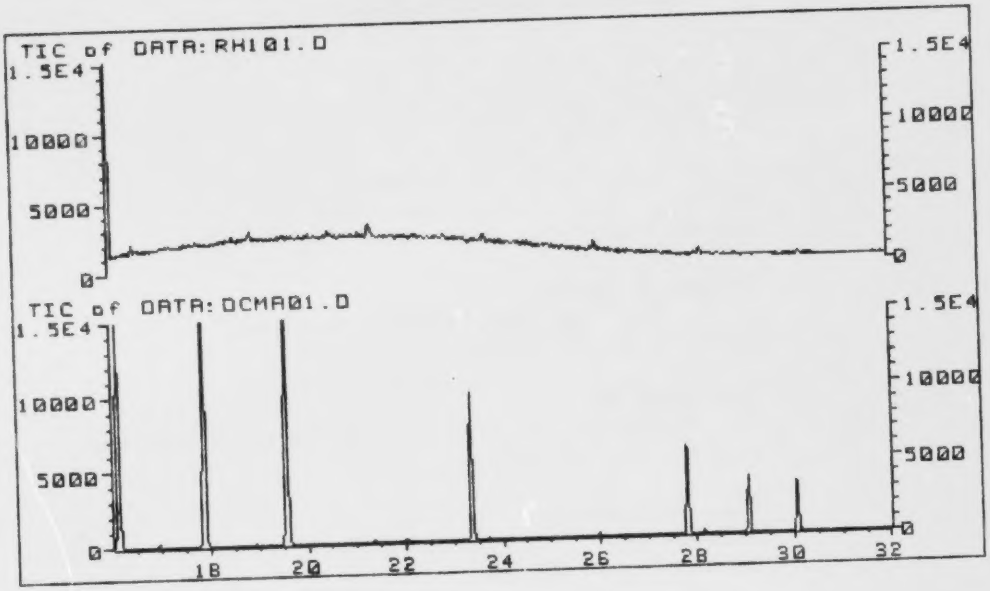


Figure 3

UPPER: Guam soil after treatment.

LOWER: CDMA PCB mixture
(left to right = tetra, penta, hexa at 10 ppm
and hepta, octa, nona and deca chlorobiphenyl at 5 ppm.)

DEMETALLATION OF USED OIL TO FACILITATE USE AS A NON-HAZARDOUS FUEL

By: **J. H. Kang and A. R. Tarrer**
Chemical Engineering Department
Auburn University, AL 36849

Edward R. Bates
U. S. Environmental Protection Agency
Cincinnati, OH 45268

Joe Kaminski
The Office of the Assistant Secretary of Defense
Alexandria, VA 22314

Mike Dombkowski
Defense Reutilization and Marketing Service (DRMS)
Battle Creek, MI 49017

ABSTRACT

Used oil invariably contains soluble and insoluble metal-bearing compounds. The presence of these compounds complicates the recycling of used oil as a fuel, by causing boiler maintenance problems and by making it difficult to comply with particulate emission standards and RCRA regulations. Demetallating a used oil prior to its burning minimizes maintenance problems and facilitates meeting the regulatory requirements controlling its burning. Different physical and chemical methods can be used to demetallate used oils. In this work, a chemical demetallation agent was used to convert entrained non-filterable metals into a form which could be effectively removed by filtration. Two different types of chemical demetallation agents were used: metallic borohydrides ($NaBH_4$ and KBH_4) and ammonium salts (DAP, $(NH_4)_2SO_4$, etc.) The activity and selectivity of these demetallation agents under different reaction conditions in various types and sizes of reactors (thereby varying mass transfer rates) were compared in bench-scale studies as well as in pilot-plant runs. Several types of used oils having different metal contents were examined. Both sedimentation and filtration were found to be practical for removing solid metal products, with filtration rates being significantly accelerated by the addition of low percentages of No. 2 fuel oil.

KEY WORDS: Waste oil, demetallation, ash content, lead content, metallic borohydrides, diammonium phosphate, lead reduction.

Introduction

In the United States, automotive and other oil-consuming industries generate about 1.1 billion gallons of used oil each year *[1]*. This voluminuous amount constitutes a serious waste oil disposal problem. Recent Environmental Protection Agency (EPA) regulations and growing public concern over hazardous wastes make development of a viable alternative to land-filling very desirable. The objective of this work was to develop a practical and feasible waste oil demetallation process to remove the ash-forming contaminants, especially organolead compounds, from the oil so that the demetallated used oil would qualify as a specification-grade fuel oil [2].

Waste oil, although contaminated, has a high energy value. A major operation in reclaiming waste oil is the removal of water and various ash-forming impurities that remain dispersed in the used oil. The ash-forming impurities consist of very fine carbon particles, organometallic particulates (e.g., organolead compounds), and inorganic materials (e.g., dust).

Reuse of an untreated used oil having a high concentration of lead and other metallic contaminants may lead to serious air pollution and boiler maintenance problems. To qualify for minimal regulatory requirements, i.e., specification-grade fuel oil requirements under EPA regulations, the lead content of a waste oil to be recycled as a fuel in a commercial boiler can not exceed 100 ppm. Since most of the used oil from the automotive industry contains several times the permissible EPA limit, it is imperative that an economic process be developed to reduce the lead content of the oil to an acceptable level so that the reclaimed waste oil can safely be reused as a fuel oil without endangering public health or the environment.

Waste oils were demetallated using two types of demetallating reagents: metallic borohydrides and ammonium salts. First, a detailed parametric study was undertaken on a bench scale to map out the process variables so as to identify the most efficient demetallation conditions. An evaluation of solid-liquid separation techniques was also done to design an efficient solids removal operation for the subsequent pilot plant studies.

Experimental Procedure (Bench-Scale Studies)

Materials -- All oil was collected from the Auburn University Waste Oil Reprocessing Pilot Plant. The demetallating reagents used were sodium borohydride, potassium borohydride, sodium borohydride aqueous solution, diammonium phosphate (DAP), and ammonium sulfate. The phase transfer catalyst used was tri-n-butyl-methyl ammonium chloride.

Equipment -- Three types of reactors were used. They were: an autoclave (3785 ml and 300 ml), a microreactor (45 ml), and a distillation flask (300 ml). The autoclave was equipped with a turbine agitator, a cooling coil, baffles, and a thermowell, all made of 316 stainless steel. The autoclave was heated by an electric furnace and agitation was provided by a magnedrive system. The tubing bomb microreactor (TBMR) was constructed of 316 stainless steel tubing (1.9 cm O.D. with 0.165 cm wall thickness and a length of 20.3 cm). Agitation was provided by a shaker assembly as shown in Figure 1. For a typical run, the TBMR was immersed in a preheated fluidized sand bath. As for the distillation flask, the reaction mixture was agitated using a magnetic stirrer, and the reactor was heated in a constant temperature paraffin oil bath.

Analysis -- The experimental results were verified in accordance with an EPA approved quality assurance project plan. The properties of the demetallated used oil were evaluated to assess its potential as an EPA specification-grade fuel oil using the following test methods: water content, ASTM D4006-81 (Water in crude oil by distillation); ash content, a modification of ASTM D482-80 (Ash from petroleum products); lead content, standard atomic absorption (AA) analysis.

In each ash analysis, an oil specimen (about 5 g) in a preweighed crucible was dried first on a hot plate and then heated in a Model F-6000 Thermolyne muffler furnace at a rate of 373K (100°C) per hour. Once the temperature reached 873K (600°C), the crucible was allowed to stay in the furnace for an additional 12 hours. Then, the crucible was removed and cooled in a desiccator. The weight of ash remaining in the crucible was determined, and its percent concentration in the original oil sample was computed.

In each lead analysis, the ash was dissolved in an acid solution of 10 ml of HNO_3 solution (1:1) and 2 ml of concentrated HCl. The lead content was determined using AA spectroscopy. A lead working standard was prepared by serial dilution of a lead standard solution (1000 ± 1% ppm) supplied by Fisher Scientific. A blind-spiked oil sample was occasionally prepared to verify the results. An organic lead standard (lead cyclohexanebutyric acid, $[C_6H_{11}(CH_2)_3COO]_2$ Pb) was used for this purpose.

Results and Discussion

Use of Metal Borohydride As A Demetalling Reagent

The properties of metal borohydrides, such as $NaBH_4$, KBH_4, and SWS solution (consisting of 12 wt% $NaBH_4$, 40 wt% NaOH, 48 wt% water), are described in detail in technical literature published by Morton Thiokol, Inc., Ventron Division [2,3].

Metallic borohydrides (e.g. sodium borohydride) are strong reducing agents. The following reaction is typical of the metal reduction that occurs with sodium borohydride [2].

$$8MX + NaBH_4 + 2\ H_2O \longrightarrow 8M^o + NaBO_2 + 8\ HX$$

where M = the metal (valence 1^+)
X = the anion

In this chemical reaction, stoichiometrically, sodium borohydride ($NaBH_4$) has 8 reducing equivalents per molecule. Based on bench-scale experimental results, Morton Thiokol, Inc. reported that a stabilized water solution (i.e., SWS solution) was an effective reagent for removing lead from used crankcase oil [4]. It should be noted that sodium borohydride ($NaBH_4$) degrades in the presence of water or acid via hydrolysis to liberate hydrogen and a salt ($NaBO_2$) when the pH of the solution is low. A representative chemical reaction is as follows:

Water Hydrolysis:

$$NaBH_4 + 2H_2O \longrightarrow NaBO_2 + 4\ H_2$$

A parametric study was done to investigate the lead reduction efficiency of two Morton Thiokol products: Venpure powders ($NaBH_4$ and KBH_4) and SWS solution. A tubing bomb microreactor (TBMR) and the reaction conditions listed in Table 1 were used in this study. A concentrated NaOH aqueous solution (50 wt%) was usually added to maintain a high pH and thus a low hydrolysis activity of the metal borohydrides.

In a typical run, the TBMR was charged with 20 g of waste oil, the specified amounts of 50 wt% NaOH aqueous solution and VenPure product. The reactor was then sealed. Subsequently, the TBMR was attached to the vertical shaft of the agitation assembly, as shown in Fig. 1, and agitated at ambient temperature for 3 minutes at 860 rpm before lowering it into the preheated fluidized sand bath. The heat-up time was about 60 seconds. At the end of the chosen reaction time, the TBMR was removed from the sand bath, immediately quenched in cold tap water, and checked for any leaks. The gases were released slowly from the bomb under a hood and the liquid product was then collected and vacuum filtered. The filtrate (or product oil) was collected for ash and lead analyses.

With 0.65 wt% SWS and 1.2 wt% NaOH solutions, the lead content of the Type B oil was markedly reduced from 480 to 70 ppm (Run 1) as shown in Table 2. In other words, an 85.4% lead reduction was achieved. This is well within the allowable maximum lead content of 100 ppm for specification grade used oil set by EPA. However, a high sludge production (16 wt%) resulted from this run.

Since metal borohydrides are expensive, the charge of SWS solution (containing 12 wt% sodium borohydride) was reduced to 0.43 wt% in Run 2. Also, the charge of NaOH concentrated solution was reduced from 1.2 wt% to 0.8 wt%. The result was that the lead content of the oil decreased by only about 50%, to 240 ppm. The ash content of the product oil was 0.58 wt%. The amount of sludge production was about the same as that from Run 1.

In order to reduce the sludge production, in Run 3, only 0.05 wt% $NaBH_4$ powder was used and no NaOH was added. The amount of lead reduction was only 10.4 percent; however, little sludge was produced (2 wt%). To enhance the demetallation activity, 0.8 wt% of 50 wt% NaOH was added in Run 4 and the other reactions conditions were kept the same. The lead removal efficiency increased from 10.4% for Run 3 to 37.5% for Run 4.

To improve the solubility of $NaBH_4$ in the oil phase, 0.10 wt% of phase transfer catalyst (tri-n-butyl-methyl ammonium chloride) was also added to the oil (Run 5). Comparing the results of Run 5 with those of Run 3 (in both runs no NaOH was added), the addition of the phase transfer catalyst did result in an increase in lead removal efficiency from 10.4 to 27.1%. With 0.8 wt% NaOH solution added in Run 6, the lead reduction efficiency improved slightly more to 31.3 wt%. On the whole, there seemed to be a trade-off between using either SWS or $NaBH_4$ powder as a demetalling reagent; the former performed better in terms of lead reduction efficiency; whereas the latter produced less sludge.

To determine the reproducibility of the demetallation experiment, Run 1 was duplicated by Run 7, and the results were essentially the same for both runs, confirming the accuracy of the experiment.

Since waste oil is derived from various sources, it is plausible that the lead removal efficiency using a demetalling reagent might respond differently to different types of waste oil. Thus, a different oil, viz., Type A oil (lead content = 660 ppm, ash content = 0.59%) was used in Runs 8-12.

In Run 8, the reaction conditions were almost the same as those in Run 1 only a different oil was used. The lead content of Type A oil was reduced by about 24% to 500 ppm; whereas for Type B oil the lead content decreased by 85% to 70 ppm (Table 3).

When the charge of SWS was doubled (Run 9), the lead content of Type A oil was reduced by about 58% (from 660 ppm to 280 ppm) as shown in Table 4. SWS contained 12 wt% sodium borohydride, which implied that the sodium borohydride concentration in the oil in Run 9 was 1,560 ppm. A sodium borohydride concentration of this level would not be economically feasible for reclaiming waste oil.

As mentioned earlier, the runs with caustic and SWS solution were characterized by high sludge production. A gel-like product was occasionally observed, which was difficult to filter, making the determination of sludge content very difficult. The gel formation was probably due to the presence of sodium hydroxide which acts to saponify fatty acids (e.g. detergents) present in the used oil. In order to inhibit the gel formation, sodium borohydride was added in a powder form (Runs 10 and 11) instead of in a solution; NaOH was still introduced as a 50% aqueous solution to maintain the activity of sodium borohydride.

In Run 10, 0.15 wt% (i.e., 1500 ppm) $NaBH_4$ was added, which was approximately the same amount of $NaBH_4$ added in Run 9; the lead reduction efficiency was slightly lower than that of Run 9. This was probably due to the greater solubility of $NaBH_4$ in Run 9. In Run 11, a phase transfer catalyst (tri-n-butyl methyl ammonium chloride) was added, and the lead content of Type A oil was reduced by about 73% to 180 ppm.

When potassium borohydride (KBH_4) was used in Run 12, the lead reduction was 59% (i.e., from 660 to 270 ppm). Thus the final lead content was still above the 100 ppm allowable maximum limit.

Examination of the ash content of the product oil (shown in Tables 2 and 4) reveals that, for both types of waste oil, the ash content of the product oil was not markedly decreased by metal borohydride treatment, although the lead content was selectively reduced in some cases. This might be attributed to the formation of other fine salts which could not be separated by regular filtration. A major disadvantage of using metal borohydrides as a demetalling reagent is that the pH must be kept high for the borohydrides to be stable, and this results in a very viscous (gel) product.

In the previous runs, the reaction temperature used was 110°C. When the reaction temperature was increased from 110°C to 150°C, keeping the other conditions the same as those used in Run 1, the product was a gel, and as a result, poor lead reduction efficiency was obtained (Runs 13 and 14, Table 5).

Investigation of Gel Formation -- Several experiments were conducted in which a cotton seed oil or a non-detergent virgin motor oil was reacted with either SWS solution or $NaBH_4$ powder to confirm that saponification does occur when fatty acids are present.

A cotton seed oil (20g) was blended with 1.2 wt% NaOH in 50% aqueous solution, and then reacted with 0.65 wt% SWS in a TBMR (Run 15). The reaction was conducted under reaction conditions given in Table 1 (similar to those used for the TBMR demetallation runs). The reaction product was collected in a 2.5 cm O.D. x 15 cm length test tube. The sludge produced was about 35 volume % (Table 6). This sludge was probably the salt resulting from the saponification of fatty acids, in the cotton seed oil, with NaOH. The cotton seed oil was reacted with 0.05 wt% $NaBH_4$ powder in the absence of sodium hydroxide (Run 16). In this case no sludge was formed, confirming that the sludge (gel) was due to the reaction of fatty acids with NaOH. The amount of $NaBH_4$ was doubled, and still, there was no sludge formed (Run 17). The effect of NaOH on non-detergent motor oil was observed by reacting an SAE-30 non-detergent motor oil with SWS (Run 18). After the reaction, two layers of liquid were formed. The top layer was reddish brown and the bottom layer was bluish green in color. A trace amount of suspended solids was also observed. In summary, the gel product formed while treating used oil with borohydrides with NaOH present was probably due to the saponification of fatty acids.

Effect of Caustic -- In an attempt to reduce the amount of sludge production, two reactions (Runs 19 and 20, Table 7) were performed in which

1.5 wt% NH_4OH was added instead of NaOH, using the reaction conditions shown in Table 1. Also, to help stabilize the NH_4OH, 25 psig of NH_3 was used (Run 19). As compared to a 0.8 wt% NaOH addition (Run 4), the amounts of lead reduction and sludge production were about the same.

Effect of Water -- As noted earlier, the reducing ability of metallic borohydrides can be hampered substantially by water hydrolysis. Since the waste oils obtained were used as-received (which had a water content of about 5 volume %), the poor performance for those runs with metallic borohydrides, in terms of lead reduction efficiency and ash content remaining in the oil, may possibly be attributed to the presence of water during the reaction. To investigate the effect of water on lead removal, a sufficient amount of Type A oil (containing 5 vol % water) was blended with 0.25 wt% and 0.50 wt% NaOH solutions (50 wt% concentrated solution) respectively. Water along with some light ends were then distilled off via atmospheric distillation. The residual oils were termed as Type C and Type D, respectively. The properties of Type C & D oils are given in Table 8.

In Run 21, 20 g of dry Type C oil was reacted with 0.9 wt% of SWS solution in a TBMR under reaction conditions given in Table 1. As shown in Table 9, the lead content of the Type C oil was successfully reduced from 700 to 100 ppm; i.e. about 86% lead reduction was achieved. This suggests that a much better demetalling performance can be achieved with a dry oil (e.g., type C) than with a wet oil (e.g. Type A).

To further minimize the use of SWS solution, the charge of SWS solution was reduced to 0.4 wt% in Run 22. As a result, about 74% lead reduction was obtained.

In Runs 23 and 24, 0.1 wt% of a phase transfer catalyst (tri-n-butyl-methyl ammonium chloride) was added to see if the demetalling performance could be improved. Compared to run 21 (without catalyst), catalyst addition (e.g., Run 23) did not improve the results.

To study the effect of NaOH charge on lead reduction, Type D oil was used in Runs 25 and 26. The difference between Type C and Type D oil was the amount of NaOH in the oil; the latter had twice the amount of NaOH than the former (~1250 ppm). In comparison to Run 22, with the same charge of SWS solution, Run 26 gave a lower lead reduction efficiency.

On the whole, Table 9 shows that the presence of water in the oil has an adverse effect on demetallation when metallic borohydrides are used. This can be avoided by distilling off the water before the demetallation reaction. It should be noted that the results presented so far were obtained for a 45 ml tubing bomb microreactor (TBMR). Knowing that these bench-scale demetallation results were to be incorporated in the scale-up and design of the Auburn University Waste Oil Reprocessing Pilot Plant, experiments were extended to a larger batch reactor, i.e., a 3785 ml autoclave, to simulate actual operating conditions as much as possible.

As mentioned above, water can decrease the demetalling activity of metallic borohydrides. Therefore, the as-received Type A oil, containing about 5 vol.% of water, was blended with 0.25 wt% NaOH aqueous solution (50 wt%) in the following runs and then distilled to a specified temperature under atmospheric pressure. The residual oil was assumed to be moisture-free. The moisture-free oil (or dry oil) was then treated with metallic borohydride products in the one-gallon autoclave. The results are given in Table 10 and discussed below:

In Run AS1, 890 g of dry oil (lead content = 700 ppm) was reacted with 0.9 wt% of SWS solution in the 3785 ml autoclave using the reaction conditions shown in Table 11. For Run AS1, only a 37% lead reduction efficiency was obtained. The poor demetalling performance was probably due to the low distillation cut-off temperature (129°C), which resulted in a certain amount of water being left behind in the residual oil. In other words, the residual oil obtained in Run AS1 was not dry enough.

Thus, in Run AS2, the distillation cut-off temperature was further raised to 175°C. The oil and SWS solution charges to the autoclave were 900 g and 0.91 wt%, respectively, which were about the same as in Run AS1. With the same reaction conditions, the lead content of the oil was markedly reduced from 700 ppm to 25 ppm; i.e., a 96% lead reduction was obtained compared to 37% in Run AS1.

Although a promising result was obtained in Run AS2, the amount of SWS solution (containing 12 wt% $NaBH_4$) used was considerable, and hence, uneconomical. Thus Run AS2 was duplicated by Run AS3 except that the SWS solution charge was halved. As a result, only a 40% lead reduction was obtained; this suggested that more SWS solution was required, if a better demetalling performance was to be achieved.

To compare the demetalling effectiveness of SWS solution and $NaBH_4$ powder, Run AS4 was performed in which the same amount of $NaBH_4$ was used as in Run AS1 (i.e. 0.10 wt% $NaBH_4$ power) and 0.20 wt% phase transfer catalyst (tri-n-butyl-methyl ammonium chloride) were reacted with 545 g of dry oil in the autoclave. Coincidentally, the same level of lead reduction was obtained. However, with $NaBH_4$ powder (Run AS4) the product oil had a lower ash content as compared to Run AS1 with SWS solution; also, less sludge was obtained in Run AS4.

To study the demetalling ability of KBH_4 powder, Run AS4 was duplicated (Run AS5) except that KBH_4 powder was used. As shown in Table 10, the lead reduction efficiency increased from 37% to 51%, but the ash content of the oil was not altered significantly.

Since KBH_4 powder is more expensive than $NaBH_4$ powder, Run AS4 was duplicated again in Run AS6, in which the $NaBH_4$ charge was increased from 0.10 to 0.15 wt% while maintaining the rest of conditions the same as in Run AS4 to determine whether a better lead reduction efficiency could be obtained. It was found that the lead reduction efficiency increased from 37 to 71%, but the ash content of the product oil did not change appreciably, as shown in Table 10. Although the amount of $NaBH_4$ used can be further increased to improve lead reduction performance, it is uneconomical to do so when the operating costs for reprocessing waste oil are considered. Therefore, another demetalling method was explored in an effort to seek the most economical process.

Use of Diammonium Phosphate As a Demetallation Reagent

As previously described, the major problems in using metallic borohydrides as demetalling reagents were: (1) a soap-like sludge was usually formed after the reaction, which was very difficult to filter; (2) a caustic oil was produced (this could result in corrosion problems); and (3) the treated oil after filtration usually had a higher ash content than the original waste oil. Because of these problems, another demetallation process, which had been proposed by the Phillips Petroleum Company as a pretreatment step in converting waste oil into a lubricating oil was investigated [1,5]. In this process, waste oil was reacted with a demetalling reagent, diammonium phosphate (DAP) (both with and without the addition of excess water). Different types of reactors were used in this investigation to permit dominant mechanisms over different operational ranges to be identified.

In the bench scale experiments, three types of reactors were used: (1) A tubing bomb microreactor (TBMR) as described previously; (2) A 500 ml distillation flask equipped with a magnetic stirrer; and (3) A 3785 ml autoclave reactor. The TBMR was operated under closed conditions, whereas the distillation was done under open conditions; i.e. the flask was open to the atmosphere to distill off water and trace amounts of light components.

TBMR Reaction Studies

Effect of Reaction Time and Temperature -- The variation in lead content of the DAP-treated oil with reaction time was observed as shown in Figure 2. The demetallation experiments were done at 150°C. From an initial value of about 210 ppm, the lead concentration of the product oil decreased with increasing reaction time to a final value of 16.5 ppm for the 90 minute run at an 800 cpm agitation rate. From this figure, it can also be deduced that agitation has a significant effect on the lead content of the oil. For example, for a 45 minute reaction time, when the agitation rate was decreased from 800 to 400 cpm, the lead content of the treated oil increased from 70 to 125 ppm. An increase in agitation is thought to increase the interfacial contact area for reaction between the oil and aqueous reactants.

To investigate the effect of reaction time on other types of oil at various reaction temperatures, several experiments were performed in which 20g of Type B oil and 8 wt% DAP (in 40 wt% aqueous solution) were reacted in a tubing bomb microreactor at temperatures of 200°C and 250°C, for 15 to 60 minutes. The results are shown in Figure 3. With a reaction temperature of 200°C, the lead content of type B oil was reduced from 480 to 230 ppm for the 60 minutes run, i.e., a 52% lead reduction. As temperature was increased to 250°C, the lead content was further reduced to about 30 ppm (i.e. a 94% lead reduction). Consequently, it can be inferred from Figures 2 and 3 that either a higher reaction temperature or a longer reaction time or both facilitate oil demetallation, as seen in Figure 4.

Distillation Flask Reaction Studies -- Run DF1 was performed in which 60 g of Type A oil (lead content = 660 ppm, water content = 5%) and 8 wt% DAP powder were mixed and heated in the 500 ml distillation flask to 150°C and the reaction was allowed to continue for an additional hour. The heat-up time was about 70 min. During the reaction, water and trace amounts of light components were distilled off. A notable result was obtained in this run (DF1) i.e. the lead content of the waste oil was successfully decreased from 660 to 24 ppm (Table 12). In other words, a 96% lead reduction efficiency was obtained. More promisingly, the ash content of the oil was also reduced to 0.02 wt% which is much lower compared to that from metallic borohydride runs (~0.5 wt%).

One may speculate that the lead reduction obtained in Run DF1 was due to the high reaction temperature and good separation by filtration. Miller found that some part of lead can be removed just by filtration [5]. Run DF2 was thus performed in which oil A alone, without adding any DAP, was heated in a distillation flask for the same period of time as in Run DF1. The result was that only a 3% lead reduction was obtained, indicating that DAP plays a very important role in demetallation. In addition, without DAP, the ash content of the waste oil was not altered appreciably. In an attempt to reduce the DAP charge, Run DF1 was duplicated by Run DF3 except that the amount of DAP used was cut from 8 to 2 wt%. Again, a similar lead reduction (97%) was obtained.

Effect of Reactor Configuration on Lead Reduction -- Table 12 shows that satisfactory demetallation results under mild conditions can be obtained using a distillation flask as a reactor. It should be noted that the reactor was open to the atmosphere. To study the effect of the reactor configuration on the demetallation performance, a tubing bomb microreactor (TBMR) was used as a closed system reactor. The mass transfer effect for this type of reactor was also studied. A detailed discussion of the experimental results is given below.

As shown in Table 12, with 2 wt% DAP, 97% lead reduction could be obtained (Run DF3). The reaction time for this run was 1 hr. To determine the effect of the reactor configuration on lead removal, Run D1 was performed in which 20 g of the same type of oil used in Run DF3 and 2 wt% DAP were charged to a TBMR and reacted for 1 hr under a closed system. Only a 70% lead reduction was obtained in Run D1 compared to 97% in Run DF3.

In Run D2, three steel balls (1/4" diameter) were added to the TBMR in order to increase the mixing effect and interfacial contact area while maintaining the rest of conditions the same as in Run D1. The lead reduction efficiency increased from 70 to 77%. When six steel balls were added in Run D3, the lead reduction efficiency increased further to 81%.

To study the effect of water presence on lead reduction, Run D3 was duplicated by D4 in which dry oil (obtained by distilling off water from Type A oil) was used instead of wet oil (i.e. Type A oil). As shown in Table 13, the lead reduction efficiency decreased from 81 to 78%. This difference was attributed to a lower interfacial contact area available for the dry oil. It should be noted that this difference was small because of the excellent dispersion obtained in this type of reactor; a much larger difference was observed later, using a reactor (autoclave) that did not have as good particle dispersion properties.

The inconsistent results (Table 12 & 13) obtained from the two types of reactors (distillation flask and TBMR) may predominantly be due to the difference in heat-up time; i.e., for a 150°C demetallation run, the distillation flask had a much longer heat-up time (75 min) than the TBMR (1 min). In other words, some demetallation may have occurred during the heat-up.

To study heat-up effects, Run D5 was performed to duplicate Run 1 (see Table 14) except that the TBMR was preheated in the fluidized sand bath (see Figure 1) so that the total heat-up time from room temperature to 150°C was about 75 min. (It should be noted that in a typical TBMR run, the sand bath alone was preheated to 150°C before the TBMR was immersed; the heat-up time was then about 1 minute.) Table 14 shows that, with the same heat-up time as that for distillation (Table 12), a satisfactory result was obtained from Run D5; i.e. 91% lead reduction could be achieved from a TBMR run. In comparison with the lead reduction obtained from the distillation run, (91% versus 97% lead reduction), this result was acceptable for a reactor with a different configuration and mixing pattern.

As discussed above, with 75 minutes of preheating time and an additional hour for reaction (i.e. total reaction time, 2 hr), 91% lead reaction could be obtained in Run D5. It would be interesting to see what the lead reduction efficiency would be with a 2 hr reaction time, 160°C reaction temperature and a regular TBMR 1 minute heat-up time. Run D8 was thus performed and the results given in Table 14 show that about the same level of lead reduction as Run D5 was obtained.

It was thus concluded that with a total reaction time of 2 hrs at 160°C, a desirable demetallation result could be achieved for various types of reactor configurations (distillation flask or tubing bomb microreactor). This agreement is mostly due to the fact that thermodynamic equilibrium (-

complete lead removable) was achieved under these reaction conditions.

Since the distillation flask was used for the evaporation of water and light components, so that the hydroxyl phosphate droplets could shrink to facilitate removal of lead particulates, an open-type reactor such as a distillation flask (Run DF3) may be more suitable for oil demetallation as compared to a closed reactor, such as TBMR (Run D5).

To further evaluate the effectiveness of DAP demetallation with respect to the configuration of the reactor used (i.e., the importance of mass transfer), a certain amount of Type A oil (lead content = 660 ppm, water content = 5 vol%) and 1.5-2.0 wt% DAP were reacted in 45 ml, 300 ml, and 3,785 ml (i.e., 1 gallon) autoclaves, at 160°C respectively. The 45 ml microautoclave, as a matter of fact, was the TBMR (tubing bomb microreactor). The results are given in Table 15.

One should note the main difference between a TBMR and a regular autoclave in terms of agitation and heating; the former was vertically agitated; whereas the latter was horizontally stirred. The mass transfer rates in the TBMR are generally better than those in the 300 ml and 3,785 ml autoclaves [7,8]. Also, the heat-up time varied a great deal; for example,the heat-up time for a TBMR heated by a preheated fluidized sand bath was about 1 minute, whereas, for a 300 ml or a 3785 ml autoclave (heated by a electrical furnace from ambient temperature) the heat-up time was approximately 2 hours. Table 15 shows that regardless of the reactor configuration, above 90 percent lead reduction was obtained using DAP as a demetalling reagent under mild reaction conditions for a reaction time of about 2 hours. The amount of solids produced was less than 1 wt%, excluding the DAP added. These observations implied that DAP is more suitable for used oil demetallation than sodium borohydride.

Effect of Water -- As described earlier, water present at the early stage of a demetallation reaction can facilitate lead removal by making more surface contact area available for the DAP.

A comparative study was carried out using a 1-gallon autoclave. The effect of water on ash and lead removal was investigated using the reaction conditions given in Table 16. Unlike the earlier studies with a TBMR (Table 13), the dispersion of the DAP was probably much less in this reactor (a stirred autoclave).

In Run AD1, with dry oil obtained by distilling off water from Type A oil, and 4 wt% DAP, a 74% lead reduction was obtained as shown in Table 17; the ash content of the product oil from this run was 0.310 wt%.

To discern the effect of water on the demetalling performance, Run AD1 was duplicated by AD2, except that a wet oil (i.e., Type A oil) was used. As a result, 99.7% lead reduction was achieved and the ash content of the product oil was very low (0.020 wt%). This observed increase in lead removal efficiency that resulted with the addition of water was significantly larger than that observed before with a TBMR and was felt to be due to the difference in the mass transfer characteristics of the reactors; namely, the degree to which the DAP was dispersed.

In Run AD3, the DAP charge was reduced from 4.0 to 1.5 wt% to reduce the operating cost and sludge generation and one part of the top of the autoclave was opened to vent water and the lights to facilitate lead removal. In so doing, the lead reduction was 98.8% and ash content was 0.030 wt%. It should be noted that for all the DAP runs, the sludge generation, excluding the DAP added, was no more than 1 wt%. A duplicate run was done in AD4 and similar results were obtained as evidenced in Table 17.

Examination of the demetallation results (Runs AD1-AD4) for Type A oil as shown in Table 17 reveal that: 1) much better lead and ash removal could be achieved when used oil contained a certain amount of water (apparently, the water aids in dispersing the DAP during initial period of reaction); 2) total metal contaminant content (i.e. ash content) was successfully reduced to an acceptable level (< 0.1 wt%); 3) a good quality of product oil could be produced with only 1.5 wt% diammonium phosphate (DAP) under mild reaction conditions; and 4) reproducibility of the DAP demetallation experiment seemed to be acceptable.

Other types of used oils (Type B & E) were also investigated using the same operating conditions as Run AD3. The lead contents for Type B and Type E oils were 480 ppm and 180 ppm, respectively and the ash contents were 0.52 wt% and 0.65 wt%, respectively.

For Type B oil, a 96% lead reduction was obtained in Run AD5 while a 99% lead reduction was obtained for Type E oil in Run AD6. The ash content of the product oil from both the runs was very low. Table 17 also shows that with 1.5 wt% DAP treatment, used oil (e.g. Type A, B, or E) seemed to be fairly well demetallated.

Use of Ammonium Sulfate as a Demetallation Reagent

Another promising ammonium reagent investigated was ammonium sulfate, $(NH_4)_2SO_4$. However, due to time constraints these experimental studies were limited to a 300 ml distillation flask equipped with a magnetic stirrer. The flask was open to the atmosphere to permit the escape of water and trace amounts of light components.

Effect of Reagent (i.e., $(NH_4)_2SO_4$) Amount on Product Oil Lead Content -To study the efficacy of ammonium sulfate, different amounts of 30 wt% ammonium sulfate solution in water were added to the waste oil as a demetallation reagent. The reaction was carried out in a 300 ml distillation flask for 1 hour at 160^0C. The results, as seen in Table 18, are extremelly encouraging. With 2 wt% of the reagent, the lead content of the product oil was substantially reduced (approx. 96% reduction) from 660 ppm to 25 ppm. This final lead content is well within the maximum permissible limit of 100 ppm for specification grade used oil. Another favorable outcome of these experiments was the low sludge production (<1 wt%).

Effect of Temperature on Product Oil Lead Content -- As was the case with other demetallation reagents, as the temperature was increased - the reaction rate increased and consequently the product oil lead content decreased substantially, for a fixed reaction time of 1 hour. Table 19 lists these results, showing the effect of temperature on the final lead content of the treated oil.

In conclusion it can be said, that in comparison with DAP, ammonium sulfate seems to be just as potent in demetallation, producing a low, quantity of non-caustic, sludge. Ammonium sulfate is however considerably less expensive than DAP, making its usage more attractive economically. Hence, additional studies investigating its demetallation efficiency were performed in the pilot-plant.

Liquid-Solid Separation Studies -- The objective of these studies was to evaluate the responses in terms of separation ease to the addition of filter aid and the use of a diluent (No. 2 fuel oil). As has been done throughout this work, both gravity sedimentation and filtration were studied for removing solids.

Two DAP demetallation runs (Runs AD8 and AD9) were performed in a 3785 ml autoclave to study the effects of filter aid and diluent on the settling time and filtration rates. The response of ash and lead content of the DAP-treated oil to the settling time were obtained. The effects of dilution with No. 2 fuel oil on settling time and filtration rate were also studied. In Run AD8, 1 wt% filter aid (diatomaceous earth) was added to the reactor with 700 g of Type A oil and 2 wt% DAP before the DAP reaction, whereas, in Run AD9, the same amount of the filter aid was added after the DAP reaction.

Table 20 shows that an oil of better quality was obtained by adding 1 wt% filter aid before the DAP demetallation (e.g. Run 8) if gravity sedimentation was adopted; for example, in Run AD8, after 24 hour of settling at 60°C without any diluents, the lead content of the product oil (i.e., top-layer oil) was greatly reduced from 660 to 20 ppm (i.e., 97% lead reduction), whereas, in Run 9, with the addition of 1 wt% filter aid after the DAP reaction, the lead content of the product oil was reduced from 660 to 46 ppm (i.e., 93% lead reduction). A higher ash content for the product oil was also obtained when the filter aid was added after the reaction (e.g., Run AD9) as seen in Table 20. When filtration was used, both runs produced a similar oil quality. In comparison with gravity sedimentation, the solids removal efficiency with filtration was higher. However, with gravity sedimentation, the product oil had acceptable ash and lead contents, and this method does have its advantages in lower operation and maintenance costs.

With filtration a good solids-removing efficiency was obtained; however the filtration rates were very low for DAP-treated used oil. In order to evaluate the use of a diluent (No. 2 fuel oil) to improve filtration rates, another DAP demetallation run was carried out in a 1000 ml distillation flask under the reaction conditions shown in Table 12 (Run DF3). After the reaction, the reaction product including spent DAP was evenly divided into four fractions; a specified amount of filter aid or No. 2 fuel oil or both were thoroughly blended in three of the four fractions. Viscosity of each fraction was first measured using a Cannon-Manning viscometer before filtration (using the house vacuum). The filtration rate for each fraction was determined, and so was the viscosity of the filtrate from each fraction. The results showed that the viscosity of the product oil drastically decreased from 90 to 33 cP at 25°C when diluted with 20% No. 2 fuel oil by weight of total liquid as shown in Table 21 (No. 2 fuel oil has a viscosity of 3.5 cP at 25°C). The filtration rate, after dilution, approximately doubled (from 11.5 to 25.0 ml/min). With the addition of 1% by weight of the total liquid, the filtration rate was further increased from 25.0 to 34.0 cm^3/min; however, the viscosity of the resulting liquid increased from 32.8 to 38.4 cP due to the presence of extra solids (i.e., filter aid).

Conclusion (Bench-Scale Studies)

Used oil treated with $NaBH_4$ aqueous solution (i.e., SWS solution) was characterized by high sludge production and ash content. High sludge production could be circumvented by substituting SWS solution with $NaBH_4$ or KBH_4 powder. However, the lead reduction efficiency decreased. Demetallation performance with metal borohydride treatment could be greatly improved by distilling off water contained in the used oil before the reaction.

As for DAP demetallation, water present (about 5 wt%) during the early stages of the demetallation reaction was found to be beneficial. This beneficial effect was felt to be due to the additional interfacial contact area available for DAP particles to react with oil. Overall, mass transfer (DAP dispersion) was observed to be important; however, by extending the reaction time (≈ 2 hr), even with mild reaction conditions, thermodynamic equilibrium (≈ 100% lead removal) could be approached, thereby minimizing the significance of any mass transfer related parameters. Ammonium sulfate seemed to be just as efficacious as DAP, without producing a large amount of sludge. It is also more attractive economically than DAP, however, to date the range of experiments using it have been more limited.

In liquid/solid separation, a better quality of oil was obtained by filtration as compared to gravity sedimentation. (Nevertheless, an EPA specification-grade oil was produced using gravity sedimentation.) The oil filtration rate was doubled by dilution with 20 wt% of No. 2 fuel oil.

Pilot Plant Studies

Pilot plant studies have been subdivided into two stages. The ongoing intermediate pilot plant studies which have recently begun constitute the first stage. The magnitude (in terms of through-puts, reactor sizes etc.) of this stage is more limited. The principal objective of the intermediate pilot plant study is to ascertain the reproducibility of data gathered from the bench scale studies. Of particular importance is the role of mass transfer or interfacial surface area between the aqueous and organic phases. To this end, studies, using the previously mentioned demetallation reagents, are directed toward determining the importance of the dynamics of water removal rates versus reaction rates. The second stage of pilot plant testing will be the operation of the final pilot plant. Its principal objective is to fine tune the demetallation process to define the optimum operating parameters and demetallation reagent.

Process Description of the Intermediate Pilot Plant

Used oil from the feed tank (ST-1) is pumped into the two mixing tanks (MK-1, MK-2). MK-1 has a volume of 14 gallons whereas MK-2 holds 85 gallons (Refer to fig. 5). In the mixing tanks, oil is thoroughly mixed with an aqueous solution (30 wt.%) of the demetallation agent (DAP or $(NH_4)_2SO_4$). The DAP solution constitutes about 2 wt% of used oil. Mixing is achieved by an electrical agitator. Oil to be demetallated is feed to the reactor from MK-2 by means of a metering pump. The contents of MK-1 serve as a back-up for MK-2, in the event that MK-2 runs dry. The demetallation reactor is a continuously stirred tank reactor (CSTR). The reactor vessel has a total volume of 30 gallons. It is heated by means of a gas burner at the bottom and is provided with a variable speed agitator. During operation, the reactor temperature is maintained at 320°F, while the pressure is atmospheric. A feed rate of 7.5 gallons/hr is used to permit a 2 hour residence time in the reactor. The reactor is adequately insulated to minimize heat loss. During reaction a small fraction of volatile components is recovered in a condensation unit and the reaction product (i.e., demetallated oil) is pumped via a metering device to a 120 gallon settling tank (SL-1). The settling tank facilitates separation of the product oil from the solid waste sludge material. The product oil is subsequently stored in a storage tank, whereas the sludge material, withdrawn from the bottom of the settling tank, is stored in drums prior to its disposal.

Results from Intermediate Pilot Plant Studies

Initially, the biggest impedement in this scale-up operation was the foaming of oil (>50 vol.%) in the reactor. This caused substantial loss of oil as it would exit the reactor in the form of slugs and foam via the outlet for the lights and flood the condensor. It is felt that the foaming was due to rapid vaporization of lights resulting from a high heat-up rate caused by the direct heating of the reactor; the vapor velocity in the linch line between the reactor and the vapor fractionation column was estimated to be 70 ft/sec.

To circumvent this problem various design changes were incorporated. As a first step, the reactor agitator was fitted with lateral wire like filaments at various heights along the agitator shaft. These filaments partially helped break the foam in the reactor itself. A second modification, was the introduction of a larger tappered cylindrical column through which the lights, and escaping foam, would have to pass prior to reaching the condensor. This column was 4 ft. long, with a top diameter of 1.5 ft. and a bottom diameter of 1 ft. The column was packed with ceramic packings at the bottom and fitted with mechanical foam arrestors at regular intervals along its height. These mechanical defoamers were wire meshes (screens) attached to the column wall. A recycle line fitted to the bottom of the column directed the defoamed oil back to the reactor.

With the above modifications in place demetallation reactions were carried out. No foaming occurred with excellent demetallation and deashing resulting. These results are tabulated in Table 22. Complete material balance data are also shown in Table 22.

Final Pilot Plant Description

The principal units of the final pilot plant, which is designed for a through-put of 3 gallons per minute of waste oil, consist of the storage facility, the demetallation units, the separation units and the waste water treatment facility. These basic units, shown in Figure 6, are described below.

The storage facility includes separate storage tanks for the untreated waste oil, light fuel oil recovered as a distillate from the demetallation process, and heavy fuel oil (i.e. the demetallated used oil). Drums to store the solid sludge-material produced from the demetallation process constitute the remainder of the storage facility.

The demetallation unit consists of a screen filter to arrest dirt to avoid clogging of the heat exchanger tubes in the pre-heater, a gas fired pre-heater to heat the used oil to the reaction temperature, a continuous stirred tank reactor (CSTR) in which the demetallation reaction takes place, and a light duty condensor to capture the volatile organics leaving the top of the reactor.

The separation unit consists of a distillate tank to separate the lights from waste water, a sedimentation unit to facilitate separation of the demetallated oil from the oily sludge, a plate and frame filter press which serves as a final step in removing any solid particles from the product oil, and two skim/wash tanks in series to enable recovery of as much entrapped oil as possible from the oily sludge material.

The waste water treatment facility incorporates two treatment tanks. The first tank facilitates precipitation of soluble contaminants (inorganic and organic) by chemical reaction with reagents, whereas the second involves biological treatment of the waste water to comply with municipal BOD and COD requirements prior to its discharge to a sewer.

Results from Final Plant Studies

It is expected that the pilot plant tests will be completed during the Fall of 1988 and the results published during the spring or summer of 1989.

Demetallation Process Waste Disposal Options

The solid waste extracted from the demetallation process is concentrated with heavy metals and consequently, is classified as an EP Toxic hazardous waste. Added to this, growing public environmental awareness, coupled with constantly emerging stricter regulations, make the disposal of this waste from the demetallation process a subject of immense importance. Nevertheless, a couple of viable options that afford a safe way of disposing of this waste do exist.

1) Despite the high concentration of some heavy metals in the sludge, it does have sufficient fuel value (>5,000 Btu/lb) and hence would qualify as a hazardous waste fuel. The waste could therefore be burned in approved cement kilns by blending, in a low ratio, with virgin fuel. A number of other industrial furnaces, such as, lime kilns, coke ovens, blast furnaces, aggregate kilns, phosphate kilns etc., are also authorized to burn such hazardous waste fuel.

2) The sludge could be treated to extract all residual, entrapped oil, allowed to dry to form a hardened cake, and then be disposed of in drums at permitted landfills.

Acknowledgements

The authors would like to thank Morton Thiokol, Inc. for providing metal borohydride chemicals. The information in this document has been funded in part by the United Stated Environmental Protection Agency (EPA) under cooperative agreements CR 812090 and CR 814635 and by the Department of Defense under interagency grant RW 97931972 to Auburn University.

References

[1] M.M. Johnson, "Reclaiming Used Oil by Chemical Treatment with Ammonium Phosphate," U.S. Patent 3,879,282, 22 April 1975.

[2] Code of Federal Regulations, Title 40, Part 266.40.

[3] Process Stream Purification With Sodium Borohydride Technical Manual and Users Guide, Morton Thiokol, Inc., Ventron Division.

[4] Metal Removal & Recovery With Sodium Borohydride, Morton Thiokol, Inc., Ventrol Division.

[5] Personal communication with Ventrol Division of Morton Thiokol, Inc.

[6] Miller, T.M., "An Investigation of the Demetallization Chemistry Associated with the Re-refining of Used Motor Oil," M.S. Thesis, North Carolina State University, Raleigh, N.C. (1983).

[7] "The Use of Disposable Catalysts in Coal Liquefaction Activities for Oil Production", presented at the National AIChE Meeting, Houston, Texas, March, 1981.

[8] Gollakota, S.R., "An Investigation of Mass Transfer Phenomena in Coal Liquefaction: Assessment of Resistances and Reactor Types," Ph.D. Dissertation, Auburn University, Auburn, AL (1984).

Table 1--*Reaction conditions for typical TBMR runs*

Demetallation reagent	Metallic Borohydrides	DAP
Reaction temperature, °C	110, 150	150-160
Heat-up time, sec	60	60
Reaction time, hr	2.0	0.5-2.0
Agitation rate, cpm	860	860

Table 2--*Demetallation results using metal borohydrides (for type B oil)*

Run No.	1	7	2	3	4	5	6
50% NaOH Added to the Oil[a], wt%	1.2	1.2	0.8	0	0.8	0	0.8
SWS, wt%	0.65	0.65	0.43	0	0	0	0
$NaBH_4$ Powder, wt%	0	0	0	0.05	0.05	0.05	0.05
Phase Transfer Catalyst[b], wt%	0	0	0	0	0	0.1	0.1
After Reaction:							
Sludge Production, wt%	16	16	15	2	-	6	7
Product Oil Analysis:							
Ash Content, wt%	0.36	0.36	0.58	-	0.77	0.40	0.53
Lead Content, ppm	70	69	240	430	300	350	330
Lead Reduction, %	85.4	85.6	50.0	10.4	37.5	27.1	31.3

[a] Oil charge = 20g Oil Type: B (lead content = 480 ppm, ash content = 0.52 wt% water content = 1.8 vol%).

[b] Tri-n-butyl-methyl ammonium chloride.

Table 3--*Effect of oil type on demetallation*

Run No.:	1	8
Oil Type	B	A
Lead Content, ppm	480	660
Oil Charge, g	20	20
50% NaOH Added to the Oil, wt%	1.2	1.2
SWS, wt%	0.65	0.65
Product Oil Analysis:		
Ash Content, wt%	0.36	0.57
Lead Content, ppm	70	500
Lead Reduction, %	85.4	24.2

Table 4--*Demetallation results using metal borohydrides (for type A oil)*

Run No.	8	9	10	11	12
50% NaOH. Added to the oil[a], wt%	1.2	1.2	1.8	1.8	1.8
SWS, wt%	0.65	1.3	0	0	0
KBH_4 Powder, wt%	0	0	0	0	0.15
$NaBH_4$ Powder, wt%	0	0	0.15	0.15	0
Phase Transfer Catalyst[b], wt%	0	0	0	0.10	0.35
Product Oil Analysis:					
Ash Content, wt%	-	0.62	0.56	0.50	0.68
Lead Content, ppm	500	280	300	180	270
Lead Reduction, %	24.2	57.6	54.5	72.7	59.1

[a] Oil charge = 20 g Oil Type: B (lead content = 660 ppm, ash content = 0.59%, water content = 5 volume %).

[b] Tri-n-butyl-methyl ammonium chloride.

Table 5--*Effect of reaction temperature on sludge formation*

Run No.:	1	13	14
Oil Type	B	B	B
Reaction Temp., °C	110	150	150
50% NaOH, wt%	1.2	1.2	1.2
SWS in the oil, wt%	0.65	0.65	0.65
After Reaction:			
Sludge Production, wt%	15.5	100% (Gel)	100% (Gel)
Product Oil Analysis:			
Lead Content, ppm	70	400	-
Lead Reduction, %	85.4	16.7	-

Table 6--*Effect of caustic solution on gel formation*

Run No.:	15	16	17	18
Oil Type	Cotton Seed Oil[a]	Cotton Seed Oil	Cotton Seed Oil	Motor Oil[b]
50% NaOH in the oil, wt%	1.2	0	0	1.2
SWS, wt%	0.65	0	0	0.65
$NaBH_4$ Powder, wt%	0	0.05	0.10	0
After Reaction:				
Sludge Production, Vol%	35	0	0	trace[c]

[a] Made from winterized cotton seed oil with TBHQ and citric acid in propylene glycol to retard oxidation with dimethylpolysiloxane added as an antifoaming agent. Made by Lou Ana Foods, Inc., Opelousas, LA 70570.

[b] GRC, G-100 Non-Detergent Motor Oil, SAE-30, made from Gurley Refining Company, Memphis, Tennessee 38101.

[c] Two phases were formed with the top layer in reddish-brown and the bottom layer in dark bluish-green with trace amount of suspended particle.

Table 7--*Influence of NH_4OH on sludge production*

Run No.:	4	19	20
Oil Type	B	B	B
Oil Charge, g	20	20	20
50% NaOH, wt%	0.8	0	0
NH_4OH, wt%	0	1.5	1.5
$NaBH_4$ Powder, wt%	0.05	0.05	0.05
NH_3, psig	0	25	0
Before Reaction:			
Lead Content, ppm	480	480	480
Ash Content, wt%	0.52	0.52	0.52
After Reaction:			
Sludge Production, wt%	4.3	3.4	3.2
Product Oil Analysis:			
Ash Content, wt%	0.77	0.31	0.37
Lead Content, ppm	300	260	400
Lead Reduction, %	37.5	45.8	16.7

Table 8--*Properties of used oils*

Oil Type	A	B	C	D	E
Water content, vol.%	5.0	1.8	0	0	0.8
Ash content, wt.%	0.59	0.52	0.75	1.02	0.65
Lead Content, ppm	660	480	700	640	180

Table 9--*Influence of water presence on lead removal using SWS solution*

Run no.:	9	21	22	23	24	25	26
Oil type	A	C	C	C	C	D	D
Oil charge	20	20	20	20	20	20	20
50% NaOH, wt%	1.2	-	-	-	-	-	-
SWS, wt%	1.3	0.90	0.40	0.90	0.25	0.35	0.40
Phase transfer catalyst[a], wt%	0	0	0	0.1	0.1	0	0
Product Oil[b] Analysis:							
Ash content, wt%	0.62	0.53	0.68	0.63	0.77	0.93	0.69
Lead content, ppm	280	100	180	120	300	280	220
Lead reduction,%	57.6	85.7	74.3	82.9	57.1	56.3	65.6

[a] Tri-n-butyl-methyl ammonium chloride.

[b] Sludge production in all the runs was high (about 15-20 wt%).

Table 10--*Results for 3785 ml autoclave runs using metallic borohydrides*

Run No.:	AS1	AS2	AS3	AS4	AS5	AS6
Atmospheric Distillation Conditions used for oil preparation:						
Type A[a] oil charge, g	890	1000	1000	600	600	600
50% NaOH, wt%	0.25	0.25	0.25	0.25	0.25	0.25
Distillation cut point, °C	129	175	175	150	150	150
Reaction Mixture:						
Residue[b] from distillation, g	890	900	900	545	545	545
SWS, wt%	0.90	0.91	0.46	0	0	0
$NaBH_4$ Powder, wt%	0	0	0	0.10	0	0.15
KBH_4 Powder, wt%	0	0	0	0	0.10	0
Phase transfer catalyst[c], wt%	0	0	0	0.20	0.20	0.20
Product Oil[d] Analysis:						
Ash content, wt%	0.74	0.50	0.51	0.57	0.56	0.53
Lead content, wt%	440	25	420	440	345	200
Lead reduction, %	37.1	96.4	40.0	37.1	50.7	71.4

[a] Water content - 5.0%
Lead content - 660 ppm
Ash content - 0.59%

[b] Lead content - 700 ppm
Ash content - 0.86%

[c] tri-n-butyl-methyl ammonium chloride

[d] Sludge production in all the runs was high (about 15-20 wt%).

Table 11--*Reaction conditions for 3785 ml autoclave runs*

Demetallation Reagent	Metallic Borohydrides	DAP
Reaction Temperature, °C	110	160
Heat-Up Time, hr	1.5	2
Reaction Time, hr	2	1
Agitation Rate, rpm	2000	2000

Table 12--Wet oil DAP demetallation study using distillation flask

Run No.	DF2	DF3	DF1
Type A Oil[a] charge, g	60	60	60
Water content in the oil, vol %	5	5	5
Percent DAP added	0	2	8
Product Oil[b] Analyses			
Lead Content, ppm	640	18	24
Lead reduction, %	3	97	96
Ash content, wt%	0.47	0.06	0.02

[a] Type A oil:
Lead Content = 660 ppm
Ash Content = 0.59 % (no filtration)

[b] Reaction Conditions:

Reaction temp, °C	150
Heat-up time, min	75
Reaction time, hr	1

Reaction Pressure = Atmospheric

[c] Less than 1 wt% solids (excluding DAP added) was produced in all the runs.

Table 13--*Effect of DAP dispersion (steel ball addition) for TBMR runs*

Run No.	D1	D2	D3	D4
No. of Steel Balls Added	0	3	6	6[a]
Product Oil[b] Analyses:				
Lead Content, ppm	200	153	127	156
Lead Reduction, %	70	77	81	78
TBMR Reaction Conditions:				
Reaction Temperature, °C	150			
Reaction Time, hr.	1			
Agitation, cpm	780			
Type A oil charge, g	20			
DAP added, wt.%	2			

[a] Dry Oil (lead content = 700 ppm)

[b] Less than 1 wt% solids (excluding DAP added) was produced in all the runs.

Table 14--Demetallation results for TBMR runs

Run No.:	D1	D5	D8	D9	D10
Type A oil Charge, g	20	20	20	20[a]	20
Percent DAP Added, %	2	2	2	2	2
TBMR Reaction Conditions:					
Reaction Temp, °C	150	150	160	160	200
Heat-Up Time, min	1	75	1	1	1
Reaction Time, hr	1	1	2	2	1
Agitation, cpm	800	800	800	800	800
Product Oil[b] Analyses:					
Lead Content, ppm	200	62	64	81	76
Lead Reduction, %	70	91	90	88	88

[a] Dry Oil (lead content = 700 ppm)
No. of steel balls used = 0

[b] Less than 1 wt% solids (excluding DAP added) was produced in all the runs.

Table 15--Oil demetallation using various sizes of autoclave

Run No.:	D8	AD7	AD2
Oil Type	A	A	A
Autoclave Size, ml	45	300	3,785 (1 gal)
Oil Charge, g	20	60	554
DAP Added, wt%	2	2	1.5
Reaction Conditions:			
Reaction Temp, °C	160	160	160
Heat-Up Time, hr	0	2	2
Reaction Time, hr	2	1	1
Reaction Pressure, psi	N/A	150	atmospheric
Agitation, rpm	800	2000	2000
Product Oil[a] Analysis:			
Lead Content, ppm	64	21	2
Lead Reduction, %	90.0	96.8	99.7

[a] Less than 1 wt% solids (excluding DAP added) was produced in all the runs.

Table 16--*Reaction conditions for 3785 ml autoclave run using DAP*

Temperature - 160°C
Heat-Up Time - 2 hr
Time - 1 hr
Agitation - 2000 rpm

Table 17--*DAP demetallation study using 3785 ml autoclave*

Run No.[a]:	AD1	AD2	AD3	AD4	AD5	AD6	AD7
Oil Type	A[b]	A	A	A	B	E	A[b]
Oil Charge, g	541	554	554	554	554	554	560
Percent DAP Added, %	4.0	4.0	1.5	1.5	1.5	1.5	1.5
Product Oil[c] Analyses:							
Lead Content, ppm	180	0	0	2	18	2	580
Lead Reduction, %	74.3	100	100	99.7	96.3	98.9	17.1
Ash Content, wt%	0.310	0.020	0.030	0.026	0.016	0.036	0.464

[a] Runs AD1 And AD2: The autoclave was completely sealed.
Runs AD3-7: One port of the autoclave was intentionally opened to allow the water vapor to escape in an effort to simulate the distillation process.

[b] Dry Oil: Lead Content - 700 ppm

[c] Less than 1 wt% solids (exlcuding DAP added) was produced in all runs

Table 18--*Demetallation with ammonium sulfate using distillation flask (300 ml)*

Run No.:	AS1	AS2	AS3
Type A Oil Charge, g	100	100	100
Ammonium Sulfate Reagent[a] Added, %	1.0	1.5	2.0
Reaction Conditions:			
Reaction Temp, °C	160	160	160
Reaction Time, hr	1	1	1
Product Oil[b] Analyses:			
Lead Content, ppm	300	60	25
Lead Reduction, %	55	91	96

[a] Ammonium sulfate was added as a 30 wt% solution in water

[b] Less than 1 wt% sludge was produced in all runs

Table 19--*Effect of temperature on final lead content using ammonium sulfate in distillation flask (300 ml)*

Run No.	AS4	AS5	AS6
Type A Oil Charge, g	100	100	100
Ammonium Sulfate Reagent[a] Added, %	2.0	2.0	2.0
Reaction Conditions:			
Reaction Temp, °C	100	130	160
Reaction Time, hr	1	1	1
Product Oil[b] Analyses:			
Lead Content, ppm	475	60	25
Lead Reduction, %	28	91	96

[a] Ammonium sulfate was added as a 30 wt% solution in water

[b] Less than 1 wt% sludge was produced in all runs

Table 20--*Effect of filter aid and/or diluent on oil quality*

Run No.:	AD 8		AD 9	
I. Sedimentation in 60°C: Water bath for 24 hr	Ash Content, wt%	Pb Content, ppm	Ash Content, wt%	Pb Content, ppm
Oil only			0.066	52
Oil+1 wt% filter aid	0.046	20	0.124	46
Oil+20 wt% No. 2 fuel oil			0.050	36
Oil+1 wt% filter aid + 20 wt% No. 2 oil	0.012	10	0.066	32
II. Vacuum Filtration:				
Oil only			0.012	4
Oil+1 wt% filter aid	0.012	0	0.014	6
Oil+20 wt% No. 2 fuel oil			0.004	2
Oil+1 wt% filter aid+20 wt% No. 2 fuel oil	0.008	0	0.002	4

Table 21--*Effect of filter aid and diluent on filtration rate and oil viscosity*

	Viscosity at 25°C (cP)	Filtration Rate (ml/min)	Filtrate Viscosity at 25°C (cP)
Oil Only	89.9	11.5	87.7
Oil + 1 wt% Filter Aid	95.5	12.0	87.3
Oil + 20 wt% No. 2 Fuel Oil	32.8	25.0	37.3
Oil + 20 wt% No. 2 Fuel Oil + 1 wt% Filter Oil	38.4	34.0	37.6

Table 22--*Batch run of intermediate pilot unit: Percentage removal of ash and lead*

Oil Charge, g	18
DAP Soln.[a] Added, wt.%	2
Before Reaction:	
Lead Content, ppm	155
Ash Content, wt.%	0.4
Reaction Conditions:	
Temperature, °F	300
Pressure, atm.	1
Reaction Time at 300°F, hr.	1
Heat-up Time, hr.	1.5
Product[b] Oil Analysis:	
Lead Content, ppm	10
Lead Reduction, %	94.5
Ash Content, wt.%	0.05
Ash Reduction, %	90

[a] DAP soln. (30 wt.% DAP, 70 wt.% H_2O)

[b] Material Balance:

Oil Balance (gal):
Input
Oil Feed = 18.8
Output
Heavy Oil Product = 16.8
Light Oil Product = 2.0
Net Losses = 0.0

Water Balance (gal):
Input
Water in Feed Oil = 1.2
Water in DAP Soln. = 0.8
Output
Water in Lights = 2.0
Net Losses = 0.0

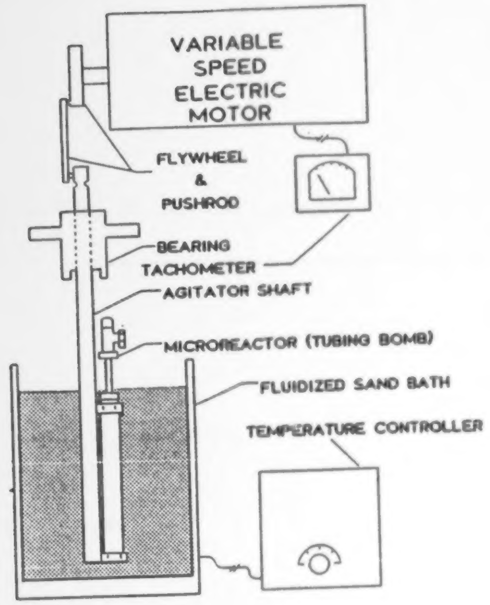

VARIABLE SPEED ELECTRIC MOTOR
FLYWHEEL & PUSHROD
BEARING
TACHOMETER
AGITATOR SHAFT
MICROREACTOR (TUBING BOMB)
FLUIDIZED SAND BATH
TEMPERATURE CONTROLLER

Figure 1 -- Schematic diagram of tubing bomb microreactor agitation assembly

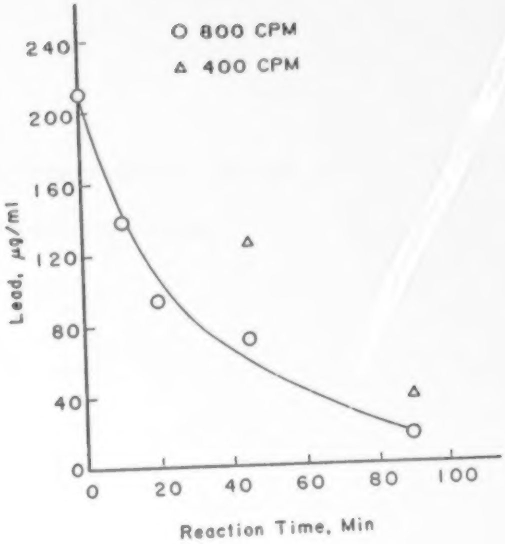


Figure 2 -- Effect of reaction time and agitation rate on lead removal

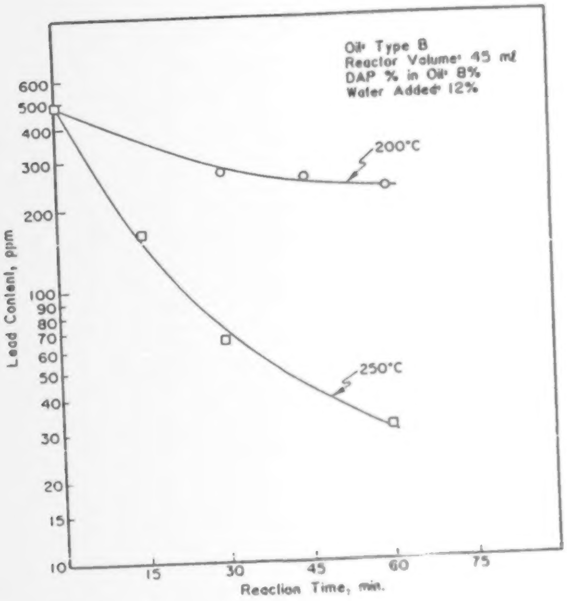


Figure 3 -- Effect of reaction time on lead removal at various temperatures

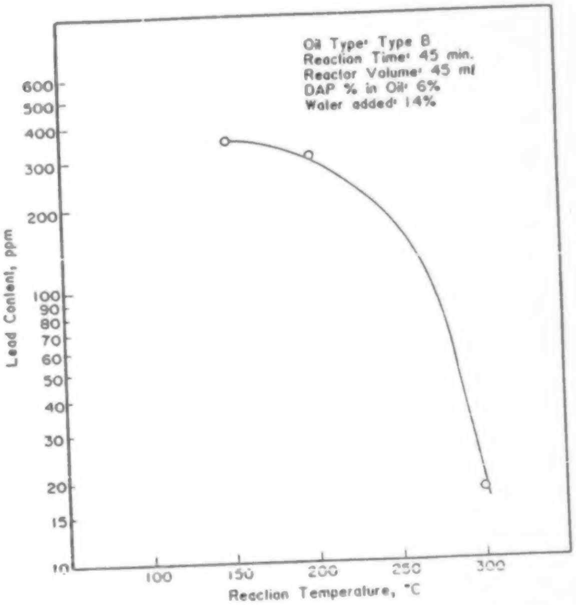


Figure 4 -- Effect of reaction temperature on lead removal for type B oil

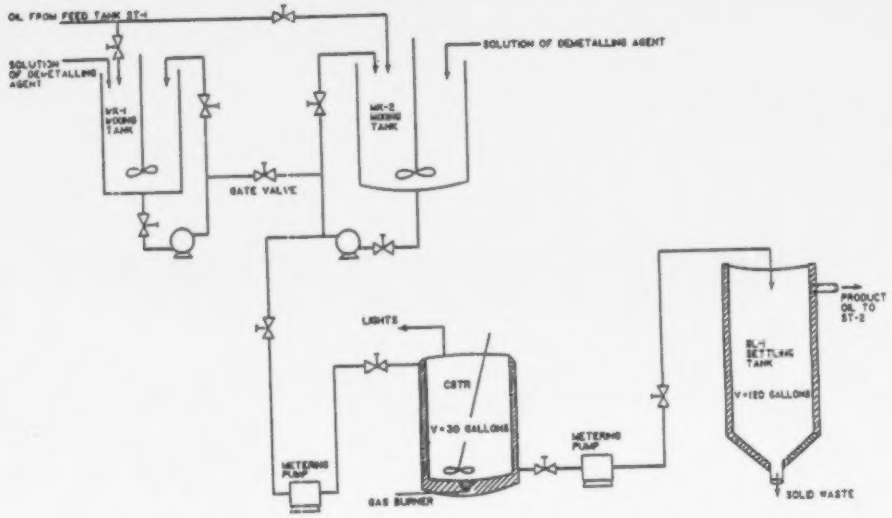

OIL FROM FEED TANK ST-1
SOLUTION OF DEMETALLING AGENT
MX-1 MIXING TANK
MX-2 MIXING TANK
SOLUTION OF DEMETALLING AGENT
GATE VALVE
LIGHTS
CSTR
V = 30 GALLONS
METERING PUMP
GAS BURNER
METERING PUMP
SL-1 SETTLING TANK
V = 120 GALLONS
PRODUCT OIL TO ST-2
SOLID WASTE

Figure 5 -- Intermediate pilot-plant flowsheet

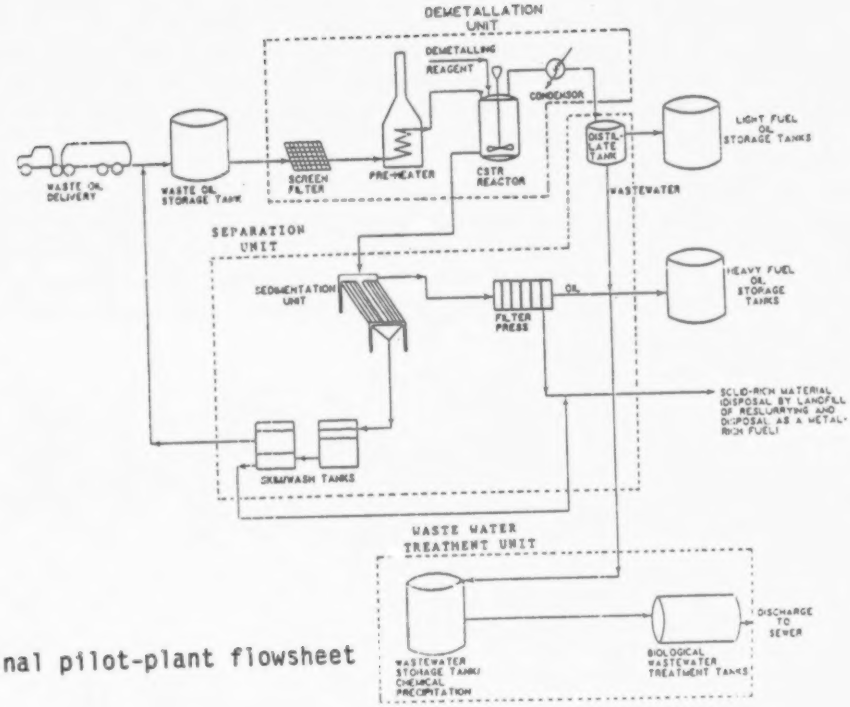

DEMETALLATION UNIT
DEMETALLING REAGENT
CONDENSOR
WASTE OIL DELIVERY
WASTE OIL STORAGE TANK
SCREEN FILTER
PRE-HEATER
CSTR REACTOR
DISTIL-LATE TANK
LIGHT FUEL OIL STORAGE TANKS
WASTEWATER
SEPARATION UNIT
SEDIMENTATION UNIT
FILTER PRESS
OIL
HEAVY FUEL OIL STORAGE TANKS
SOLID-RICH MATERIAL (DISPOSAL BY LANDFILL OF RESLURRYING AND DISPOSAL AS A METAL-RICH FUEL)
SKIM/WASH TANKS
WASTE WATER TREATMENT UNIT
WASTEWATER STORAGE TANK/ CHEMICAL PRECIPITATION
BIOLOGICAL WASTEWATER TREATMENT TANKS
DISCHARGE TO SEWER

Figure 6 -- Final pilot-plant flowsheet

THE INCOMPLETE COMBUSTION OF CARBON TETRACHLORIDE DURING NORMAL/ABNORMAL HAZARDOUS WASTE INCINERATION

by: Robert C. Thurnau
U.S. Environmental Protection Agency
Cincinnati, Ohio 45268

ABSTRACT

Land disposal of hazardous waste is the subject of the requirements of Subtitle C of the Resource Conservation and Recovery Act (RCRA) of 1976. This act requires that the treatment, storage or disposal of hazardous waste be carried out in accordance with the RCRA regulations. Incineration of hazardous waste falls under these regulations and is covered by the permitting requirements. When used for hazardous waste treatment, incineration must demonstrate that at least 99.99% of the principal organic hazardous components (POHC) are destroyed. However, as efficient as incineration is at destroying POHCs, by-products of combustion are formed and in some cases may be just as much of a health hazard as the parent compound.

The incineration of carbon tetrachloride has been successfully demonstrated at numerous hazardous waste incinerators. One of the products of incomplete combustion of carbon tetrachloride is chloroform and this paper presents a comparison of the observed chloroform values with those predicted from the unimolecular thermal decomposition reaction for carbon tetrachloride.

INTRODUCTION

The disposal of hazardous waste on land is the subject of Subtitle C of the Resource Conservation and Recovery Act (RCRA) of 1976 and its subsequent Amendments in 1984. These statues require that the storage or disposal of hazardous waste be carried out in accordance with Federal regulations. The incineration of hazardous waste falls under these regulations which specify that in addition to particulate and HCl emission limits, incinerators must reduce specified principal organic hazardous constituents (POHCs) by at least 99.99%, based on the ratio of stack gas emissions to feed concentrations. However, it has been reported that the combustion of hazardous waste[1] even at efficiencies of 99.99% can generate products of incomplete combustion (PICs), and some of these compounds are just as undesirable as the parent compounds. This paper deals with the combustion of carbon tetrachloride and one of its thermal degradation products, chloroform.

BACKGROUND

To help comply with the statute requirements of 99.99% destruction removal efficiency (DRE), indicator compounds such as carbon tetrachloride (CCl_4) are spiked into the feedstock and incinerated along with the specified wastes. The data generated from CCl_4 spiked incinerator tests, supplies additional information on the incinerator's ability to destroy a thermally stable compound, and adds credence to the overall combustion efficiency of the POHCs.

The incineration of hazardous wastes containing CCl_4 has been documented in at least four different hazardous waste incinerators[2]. It has also been reported[3] that a family of chlorinated methane compounds (chloroform, methylene chloride dichloromethane, monochloromethane) was generated when a hazardous waste spiked with CCl_4 was incinerated. From a total mass emissions (TME) standpoint, the rate at which (PICs) are generated is important to the overall performance of the incinerator. If the mechanism and rates of formation and destruction are known, the magnitude of the PIC emissions can be determined, and controlled (if necessary) by regulating the feed materials and/or changing incinerator conditions.

UNIMOLECULAR DECOMPOSITION MECHANISM

The thermal stability of numerous organic compounds has been studied in great detail by Dellinger[4,5] and associates at the University of Dayton Research Institute. Carbon tetrachloride and chloroform are two of the compounds studied and data on pseudo-first-order kinetic activation energy and Arrhenius coefficent were determined and reported[4]. The thermodynamic work was done under laboratory plug flow reactor conditions and was not applied to full-scale incinerators. However, after an extensive review of a recently completed EPA incinerator test, it was concluded that the oxygen profiles, temperature and residence time distribution were not so radically different as to preclude the laboratory work from application to the field test data.

It was postulated that CCl_4 decomposed thermally via the rupture of the carbon/chloride bond and this reaction was characteristic of a unimolecular decomposition mechanism. During the operation of a hazardous waste incinerator, the probability of generating gas phase free radicals of this type is sufficiently large to suggest the following mechanism for the destruction of carbon tetrachloride.

$$CCl_4 \longrightarrow CCl_3 + Cl$$

$$\left.\begin{array}{l} CCl_3 + H_2O \longrightarrow CHCl_3 + OH \\ Cl + H_2O \longrightarrow HCL + OH \end{array}\right. \qquad \text{Fast}$$

The overall reaction for carbon tetrachloride can be written as:

$$CCL_4 + 2H_2O \longrightarrow CHCL_3 + HCL + 2OH \qquad \text{Eq. 1}$$

Once the chloroform has been generated, its oxidation mechanism can take over and may be represented by the following global reaction:

$$CHCl_3 + 1/2O_2 + 2H_2O \longrightarrow CO_2 + 3HCl + H_2O \qquad \text{Eq. 2}$$

The operating conditions recorded during the field test were applied to the unimolecular decomposition mechanism, and the concentration of the POHC (carbon tetrachloride) and one of the PICs (chloroform) was calculated. This information was compared with the stack data collected during the test.

EXPERIMENTAL

The test was conducted on a rotary kiln incinerator system that routinely burned both conventional and hazardous waste generated by a large petrochemical manufacturing plant. The kiln can receive solid waste, slurry feed and liquid waste. During the test the slurry feed was not used. The primary combustion chamber gases exit from the end of the kiln, and are directed upward to the secondary combustion chamber. The gases leaving the secondary combustion chamber are passed through a vertical quench section and a three stage ionizing wet scrubber before being exhausted to the atmosphere. A schematic diagram of the incineration system with its various inputs is presented in Figure 1. The following data was taken on the feedstocks presented to the kiln for incineration:

Solid Waste Feedstock

1)	Chlorinated pyridine	3,000 lbs/hr	24,000 $\frac{BTU}{lb}$
2)	Polyethylene wax		
3)	Substituted cellulose		

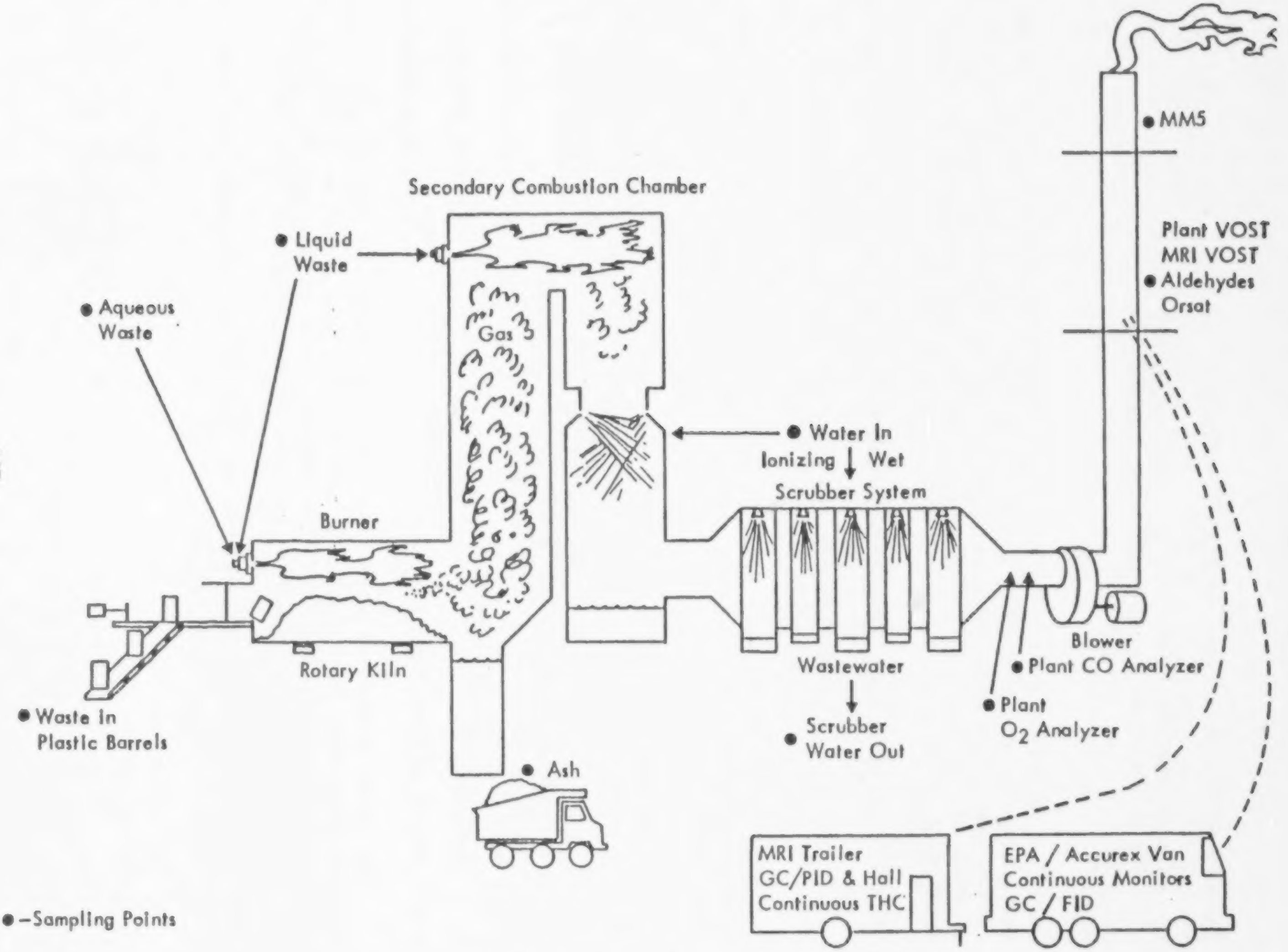

Secondary Combustion Chamber
● Liquid Waste
● Aqueous Waste
Gas
Burner
Rotary Kiln
● Waste In Plastic Barrels
● Ash
● Water In
Ionizing
Wet
Scrubber System
Wastewater
● Scrubber Water Out
Blower
● Plant CO Analyzer
● Plant O_2 Analyzer
● MM5
Plant VOST
MRI VOST
● Aldehydes
Orsat
MRI Trailer
GC/PID & Hall
Continuous THC
EPA / Accurex Van
Continuous Monitors
GC / FID
● –Sampling Points

Figure 1. Process schematic.

Liquid Waste - Organic Fraction	1341 lbs/hr @ 10.4% CCl_4	18,000 $\frac{BTU}{lb}$
Liquid Waste - Aqueous Fraction	5,000 lbs/hr @ 12.4 ppm CCl_4	15 $\frac{BTU}{lb}$

Summing up the CCl_4 input to the incinerator:

Input into the Kiln	751 grams/min
Input into the Secondary CC	1244 grams/min

RESULTS

The overall chemical reactions for the thermal destruction of carbon tetrachloride were presented earlier as a three step reaction scheme producing chloroform followed by a global oxidation mechanism producing carbon dioxide, hydrochloric acid and water. The rate expression for the disappearance of CCl_4 may be represented by the following:

$$\frac{-d\ CCl_4}{dt} = k_1\ [CCl_4][H_2O]^2 + k_2\ [CHCl_3][O_2]^{1/2}[H_2O]^2 \qquad \text{Eq. 3}$$

unimolecular reaction
pyrolysis - bond rupture

combustion - oxidation

Looking at the thermal reaction for CCl_4, utilizing Dellinger's data for the decomposition, the rate constant for the unimolecular phase can be calculated:

$$\text{rate constant} = K - Ae^{-Ea/RT} \qquad \text{Eq. 4}$$

$$k = 288{,}000\ \text{sec}^{-1}\ e^{\frac{-26{,}000\ \frac{cal}{mole}}{1.99\ \frac{cal}{mole\ °K}\ \times\ 1074°K}}$$

$$k = 288{,}000\ e^{-12.17}$$

$$k = 1.42\ (\text{for } 1550°F)\ \text{sec}^{-1}$$

A = Arrhenius Coefficient

Ea = Activation Energy

R = Gas Constant

T = Temperature °K

The other components needed for the rate expression can be calculated from the feed materials and the volume of the kiln. Based on a feed rate of 1.2 gallons/minute to the kiln, the charging rate of CCl_4 was 751 grams/min or 0.081 $\frac{moles}{sec}$. When the carbon tetrachloride was sprayed into the hot combustion chamber, its temperature was immediately elevated, thus expanding its volume.

Using the pressure, temperature and volume relationships in the Ideal Gas Law the expanded volume of 0.081 moles was calculated to be 7.23 liters. The volume of the combustion chamber was calculated as 1005ft^3 or 28462 liters, and when the carbon tetrachloride was dispersed in the combustion chamber its concentration was calculated to be 254 ppm or 2.85 x 10^{-6} moles/L.

The other variable in the pyrolysis component of the equation was the concentration of water vapor. The aqueous waste stream supplied water to the combustion chamber at the rate of 10 gallons per minute. A calculation similar to that carried out for carbon tetrachloride was done for the water component and found to be 109,000 ppm or 1.23 x 10^{-3} moles/L. The concentration of water vapor was about 400 times larger than the carbon tetrachloride, thus the limiting factor for the pyrolysis reaction was the amount of CCl_4 available for reaction. The concentration of water was assumed to be constant and was incorporated into the rate constant. Substituting these values into the rate expression and assuming first order kinetics, the amount of unreacted carbon tetrachloride remaining after undergoing unimolecular decomposition mechanism was calculated:

$$\text{rate} = \frac{-dCCl_4}{dt} = K\,[CCl_4]$$

$$\frac{-dCCl_4}{dt} = 6.12 \times 10^{-12} \text{ moles/L/sec}$$

If the decomposition rate for carbon tetrachloride is compared with the charging rate, it is found that a very small amount of the initial CCl_4 (28 ppb) was projected to remain unreacted when the combustion gases exited the incinerator. There were no samples of the incinerator exit gas taken and therefore no direct way to compare the actual carbon tetrachloride concentrations with the predicted values. It was also assumed that the chloroform formed (difference between initial and final carbon tetrachloride concentrations) was also incinerated with the rest of the waste.

The combustion gases derived from the incineration of the spiked waste material pass from the primary combustion chamber to the secondary combustion chamber where the reactions initiated in the primary are thermally encouraged to go to completion. The products of incomplete combustion generated in the kiln would be destroyed in the secondary combustion chamber with little if anything remaining in the stack gas. However, a significant amount of the spiked organic waste was also injected into the secondary combustion chamber (1244 grams/min) and the kinetics of its thermal decomposition and PIC formation would be reflected in the measurements taken in the stock.

The total volume of the secondary combustion chamber is about 6,000 ft^3, but the location of the waste injection port and the velocity of the gases reduces the effective reaction volume to about 3,000 ft^3. During the collection of the first set of samples on the volatile organic sampling train (VOST), the secondary combustion chamber was maintained at 1853° ± 31°F. Using the same approach that was applied to the CCl_4 in the primary combustion chamber, and accounting for the additional CCl_4 injected as well as the extra reaction volume, the following kinetic data can be calculated:

$$\text{rate constant} = k = Ae^{-Ea/RT}$$

$$k = 288000 \text{ sec}^{-1} \; e^{\frac{-26{,}000 \frac{\text{cal}}{\text{mole}}}{1.99 \frac{\text{cal}}{\text{mole } °\text{K}} \times 1285°\text{K}}}$$

$$k = 11.06 \text{ (for } 1853°\text{F) sec}^{-1}$$

$$[CCL_4] = 1.58 \times 10^{-6} \text{ moles/L or 142 ppm}$$

$$[H_2O] = 2.46 \times 10^{-3} \text{ moles/L}$$

Substituting the rate and concentration data into Equation #1, the amount of carbon tetrachloride left unreacted by the unimolecular decomposition portion of the overall reaction can be calculated:

$$\frac{-dCCl_4}{dt} = k^1 \, [CCl_4] \qquad k^1 = \text{pseudo first order rate constant}$$

$$\frac{-dCCl_4}{dt} = 1.06 \times 10^{-10} \text{ moles/L/sec}$$

Again, if the decomposition rate for carbon tetrachloride was compared with the charging rate, it was found that only a small portion of the initial CCl_4 remained unreacted (2 ppb) and was quenched as the gas exited the secondary combustion chamber. The stack test data collected during this test indicates a carbon tetrachloride concentration of 5 ppb and is in agreement with that predicted by the unimolecular decomposition mechanism. Table 1 compares the predicted carbon tetrachloride concentrations with the measured carbon tetrachloride concentrations for the normal operating conditions, and Table 2 summarizes the comparisons for the upset conditions.

The stack test data also showed significant concentrations of chloroform, and it is suggested that the chloroform was generated from the thermal decomposition of carbon tetrachloride. If, as the unimolecular mechanism suggests, all of the carbon tetrachloride is converted to chloroform, the same type of kinetic analysis could be carried out on the chloroform as on carbon tetrachloride and its exit concentration could also be predicted:

$$\text{rate constant} = k = Ae^{-Ea/RT}$$

$$k = 3.16 \times 10^{11}\ \text{sec}^{-1}\ e^{\dfrac{-49{,}000\ \frac{\text{cal}}{\text{mole}}}{1.99\ \frac{\text{cal}}{\text{mole}}\ ^\circ\text{K} \times 1285^\circ\text{K}}}$$

$$k = 15.06 \times 10^{2}\ \text{sec}^{-1}$$

$$[\text{CHCl}^3] = 142{,}000\ \text{ppb} - 2 = 141{,}998 = 142\ \text{ppm}$$

$$[\text{H}_2\text{O}] = 1.23 \times 10^{-3}\ \text{moles/L}$$

$$[\text{O}_2] = 1.84 \times 10^{-2}\ \text{moles/L}$$

$\text{rate} = k_1\ [\text{CHCl}_3]$ $\qquad$ k_1 = integrated rate constant

$$\text{rate} = 41.72 \times 10^{-6}\ [1.58 \times 10^{-6}]$$

$$\text{rate} = 6.592 \times 10^{-11}\ \text{moles/L/sec}$$

If the decomposition rate for chloroform is compared with the charging rate, it is found that only a small amount of chloroform (6 ppb) was predicted to remain unreacted. Table 3 compares the predicted chloroform emissions with the measured chloroform emissions taken under normal operating conditions.

Table 1. Comparison of Theoretical and Actual Carbon Tetrachloride Emissions From a Hazardous Waste Incinerator - Normal Operation

	Calculated Concentration ppb	Measured Concentration ppb
Sample 1 Pair 1	2	5
Sample 1 Pair 2	2	5
Sample 1 Pair 3	2	2
Sample 2 Pair 1	2	7
Sample 2 Pair 2	2	4
Sample 2 Pair 3	2	NA
Sample 3 Pair 1	2	2
Sample 3 Pair 2	2	1
Sample 3 Pair 3	2	1
Mean		3.4 ± 2.2

Table 2. Comparison of Theoretical and Actual Carbon Tetrachloride Emissions From a Hazardous Waste Incinerator - Operating with Periodic Upsets

	Calculated Concentration ppb	Measured Concentration ppb
Sample 4 Pair 1	2	7
Sample 4 Pair 2	3	7
Sample 4 Pair 3	2	12
Sample 5 Pair 1	1	21
Sample 5 Pair 2	1	16
Sample 5 Pair 3	2	7
Sample 6 Pair 1	1	6
Sample 6 Pair 2	1	3
Sample 6 Pair 3	1	3
Mean		9.7 ± 5.7

Table 3. Comparison of Theoretical and Actual Chloroform Emissions From a Hazardous Waste Incinerator - Normal Operation

SAMPLE	Calculated Concentration ppb	Actual Concentration ppb
Test 1 Pair 1	6	63
Test 1 Pair 2	7	51
Test 1 Pair 3	6	63
Test 2 Pair 1	2	18
Test 2 Pair 2	2	11
Test 2 Pair 3	3	NA
Test 3 Pair 1	2	72
Test 3 Pair 2	2	57
Test 3 Pair 3	1	66
Mean		50.1 ± 22.9 45.7% RSD

After the baseline experiments were completed, the incinerator was periodically operated in a way that would simulate upset or abnormal combustion conditions i.e. burner failure, barrel of concentrated waste etc. These conditions are undesirable from many standpoints, and with proper operator control usually last for short periods. The transient upset condition was simulated by spiking a large dose of waste organic solvent into the secondary combustion chamber. The upset resulted in elevated carbon monoxide and total hydrocarbon concentrations, but lasted for only 2 to 3 minutes.

The same battery of samples were collected during the upset conditions as were collected in the baseline experiments and the collected data was treated in the same manner. Table 4 summarizes the chloroform concentrations predicted by the unimolecular decomposition mechanism and the chloroform concentrations found in the stack.

Table 4. Comparison of Theoretical and Actual Chloroform Emissions From a Hazardous Waste Incinerator - Operating with Periodic Upsets

SAMPLE	Calculated Concentration ppb	Actual Concentration ppb
Test 4 Pair 1	3	75
Test 4 Pair 2	3	64
Test 4 Pair 3	3	82
Test 5 Pair 1	3	23
Test 5 Pair 2	3	31
Test 5 Pair 3	3	19
Test 6 Pair 1	7	14
Test 6 Pair 2	6	74
Test 6 Pair 3	6	21
Mean		44.8 + 28.2 63% RSD

DISCUSSION AND CONCLUSION

The application of thermal degradation data generated under closely controlled laboratory conditions to a full-scale commercial hazardous waste incinerator must be done in a careful manner. The unimolecular decomposition mechanism predicted that under both normal and upset conditions very low concentrations of carbon tetrachloride would result when waste spiked with carbon tetrachloride was incinerated. The results measured under normal conditions fit well with the predicted values, but are slightly higher for the upset conditions. The higher carbon tetrachloride values resulted when the combustion conditions in the secondary combustion chamber were altered to simulate transient upset situations.

The application of a global oxidation mechanism to the chloroform generated from carbon tetrachloride thermal decomposition also predicted that small amounts of chloroform would be present in the stack gas. The chloroform values found in the stack gas were significantly higher than predicted and may have been due to improper assumptions in the reaction mechanisms, erroneous pseudo-first-order kinetic parameters, or the assimilation of additional $CHCl_3$ from the combustion train (i.e. scrubber water).

Under normal combustion conditions the DRE for carbon tetrachloride was calculated at >99.99%. The same calculation for carbon tetrachloride under upset conditions also yielded a DRE of >99.99% and supported earlier data that suggests that upsets do not result in significant reductions in POHC DRE.

If the thermal degradation of carbon tetrachloride takes place as outlined earlier in this paper, a considerable amount of chloroform will be generated and oxidized. If the residual products of incomplete combustion ($CHCl_3$) are accounted for in the carbon tetrachloride calculation (the DRE), the level of destruction drops to 99.96% for both upset and normal combustion conditions.

The carbon tetrachloride/chloroform results summarized in Tables 1 through 4 were taken under relatively constant temperatures (1771° ± 71°F and 1805° ± 42°F). The temperature in the secondary combustion chamber was consistent between the two sets of data and should not be a significant factor in contributing to the differences observed between the emissions measured under normal and upset operating conditions.

REFERENCES

1. Trenholm, A.; Hathaway, R.; Oberacker, D.; "Products of Incomplete Combustion From Hazardous Waste Incinerators; Incineration and Treatment of Hazardous Waste", Proceedings of the Tenth Annual Research Symposium, NTIS PB 85116291, EPA-600/9-84-022, Sept. 84.

2. Castaldini, C.; Mason, H.; DeRosier, R.; Unnasch, S.; "Field Tests of Industrial Boilers Cofiring Hazardous Wastes", Hazardous Waste, Vol. 1, No. 2, 1984.

3. Trenholm, A; Thurnau, R.; "Total Mass Emissions From a Hazardous Waste Incinerator", Proceedings of the Thirteenth Annual Research Symposium, EPA-600/9-87/015.

4. Dellinger, B.; Torres, J.; Rubey, W.; Hall, D.; Graham, J. and Carnes, R.; "Determination of the Thermal Stability of Selected Hazardous Organic Compounds", Hazardous Waste Vol. 1, No. 2, 1984, p. 137-157.

5. Graham, J.; Hall, D.; Dellinger, B.; "Laboratory Investigation of Thermal Degradation of a Mixture of Hazardous Organic Compounds", Enviro. Sci. Technol. Vol. 20, No. 7, 1986, p. 703-10.

HAZARDOUS WASTE INCINERATION PRIOR TO LAND DISPOSAL

by

Ronald Turner
U.S. Environmental Protection Agency
Hazardous Waste Engineering Research Laboratory
26 W. Martin Luther King Drive
Cincinnati, Ohio 45268

and

Robert Hoye and Fred Hall
PEI Associates, Inc.
11499 Chester Road
Cincinnati, OH 45246

INTRODUCTION

The EPA's Hazardous Waste Engineering Research Laboratory (HWERL), Cincinnati, Ohio, is providing the Office of Solid Waste and Emergency Response with data on various hazardous waste treatment technologies to assist in the development of land disposal restriction standards under the Resource Conservation and Recovery Act (RCRA). Many of the RCRA listed wastes which may have been land disposed in the past are or may be incinerated. The incinerable wastes range from highly concentrated organic liquids to sludges and low-concentration solid wastes. The HWERL had collected stack gas, ash, and other analytical data from incineration of mixed RCRA and non-RCRA wastes. The purpose of the tests described in the paper is to characterize the residuals from incineration of specific RCRA wastes.

Earlier HWERL studies of incineration cases have examined the performance of combustion systems relative to destruction and removal of organics and metals in the feed. Standards have been promulgated for stack gas from hazardous waste incinerators. They require a DRE of 99.99 percent for each principal organic hazardous constituent (POHC), removal of 99 percent of hydrogen chloride from the exhaust gas, and limiting of particulate matter to 180 milligrams per dry standard cubic meter. The other two residual streams which may result from incineration are bottom ash and air pollution control device (APCD) effluent which are not specifically regulated under RCRA. Many of these residues are hazardous wastes and may also contain heavy metals and undestroyed organic material. Additional treatment may be necessary to remove or stabilize the hazardous constituents in the ash or effluents before ultimate disposal.

To determine the quality of incineration residuals, the HWERL recently sampled the ash and APCD effluents at 10 commercial facilities incinerating mixtures of hazardous wastes. Stack tests and feed sampling were not conducted. Metals, volatile, organic compounds, and semivolatile organic compounds were detected in the scrubber waters and bottom ash. Overall, the data indicated that the facilities were apparently capable of achieving high levels of RCRA organic hazardous material destruction as very small amounts of residual organic compounds remained in the incineration ash and air pollution control effluents.*

Metals such as arsenic, barium, beryllium, chromium, cadmium, lead, mercury, nickel, and zinc are of concern in incineration. The principal environmental concern is the form of the metals; i.e., bottom ash, stack emissions, or APCD residues. In general, data on metal emissions and partitioning are limited and often incomplete. Therefore, it was decided that additional tests would be necessary to characterize the organics and metals in the residues for specific RCRA waste-incinerator combinations.

This paper presents the results of a complete analysis of the feed, residues, and effluents from the incineration of two unadulterated RCRA hazardous wastes:

° K001 - Bottom sediment sludge from the treatment of wastewater from wood preserving processes that use pentachlorophenol(PCP)/rotary kiln

° K015 - Still bottoms from the distillation of benzyl chloride/liquid injection

Although K001 can consist of sludges generated from wood-preserving processes that use PCP or creosote, only the treatment of K001-PCP is discussed in this paper. K001-creosote was also incinerated in a rotary kiln test. The K001-C waste was similar to the K001-PCP in its soil and water content, but the organic concentrations and heating values were about twice as high in the creosote waste. The residual concentrations of organics and inorganics were similar to those obtained for the K001-PCP test.

---

* Van Buren, D., G. Poe, C. Castaldini. Characterization of Hazardous Waste Incineration Residuals. U.S. EPA. January 1987.

WASTE CHARACTERISTICS

K001-PCP

Wood-preserving processes that use pentachlorophenol (PCP) and creosote generate wastewater containing phenolic compounds, including penta- and tetrachlorophenol, volatile organic solvents such as benzene and toluene, and polynuclear aromatic (PNA) components of creosote. Treatment of this wastewater results in a bottom-sediment sludge (listed as K001) that must be removed for ultimate disposal. Over 170 wood treatment plants using creosote and/or PCP generate approximately 3 million gallons of wastewater treatment residuals per year.* Wood treaters periodically remove the K001 from their water treatment pond and generally send it to a hazardous waste landfill or incinerator for disposal.

The approximate concentrations of the major constituents of the untreated K001-PCP waste are given below.

Constituent	Concentration, percent
Soil	40
Water	30
Wood chips	10
Organic compounds	20 (naphthalene, phenanthrene fluoranthene, PCP, others)
	100

Significant composition parameters of the sampled K001-PCP waste are presented in the following listing. These parameters represent waste characteristics that would affect treatment performance. The wide range of values indicates the variations in composition that can be expected in K001-PCP, even from the same source.

Parameter	Range of determined values
Ash content	12 to 51% (30% average)
Heating value	3800 to 8300 Btu/lb (6000 Btu/lb average)
Water	8 to 41% (25% average)
Pentachlorophenol	920 to 3000 ppm (2000 ppm average)

A rotary kiln incinerator was used for destruction of the K001-PCP due to the semi-solid form of the waste and its high ash content.

K015

RCRA waste K015 is still bottoms generated during the production of benzyl chloride. In this process, toluene is chlorinated in the presence of ultraviolet light to produce benzyl chloride, which is then separated from unreacted toluene and refined. Two U.S. facilities generate a total of about 3 million pounds of K015 per year. The K015 is either incinerated at a RCRA permitted treatment, storage, and disposal facility (TSDF) or sold as a raw material. The approximate concentrations of the major constituents of the untreated K015 waste are indicated below.

---

* Radian Corporation. Draft Final Engineering Analysis of Wood Preservation and Surface Protection-Volume 1. Prepared for U.S. Environmental Protection Agency under Contract No. 68-01-7287, Washington, D.C. October 1986.

Constituent	Concentration, percent
Benzal chloride ($C_6H_5CHCl_2$)	88-100
Benzyl chloride ($C_6H_5CH_2Cl$)	<1
Benzotrichloride ($C_6H_5CCl_3$)	3.7-4.5
Water	<1
Other constituents	<1

Other significant parameters of the sampled K015 waste are presented below. These parameters represent waste characteristics that would affect incinerator treatment performance.

Parameter	Range of determined values
Ash content	0.01 to 0.29% (0.09% average)
Heating value	10,000 Btu/lb
Carbon	51.0 to 51.3% (51.1% average)
Dry loss	96.0 to 99.02% (97.2% average)
Sulfur	0.03 to 0.32% (0.22% average)

The K015 waste contains approximately 43 percent chlorine. It was transported to the treatment facility in 55-gallon drums. A liquid injection incinerator system was used for destruction of the K015 because of the material's high organic/low ash content.

TEST FACILITY DESCRIPTIONS

EPA COMBUSTION RESEARCH FACILITY (CRF)

The K001-PCP test burn was conducted at the U.S. EPA Combustion Research Facility located in Jefferson, Arkansas, in a pilot-scale rotary kiln incinerator rated at 2.5 million Btu/h and 1 hour retention time at 0.25 rpm. Figure 1 presents a schematic diagram of the incineration system. A ram feeder was used to inject 1.5-gallon, cylindrical fiber packs, each containing about 5 lb of the K001-PCP. The kiln is designed to operate at temperatures up to 1000°C (1832°F); however, the kiln has occasionally reached temperatures of 1150°C (2100°F).

The combustion gases from the kiln pass through an afterburner for further incineration. The afterburner's design temperature is 1200°C (2200°F), with a 2-second residence time. Both the kiln and the afterburner use propane as startup fuel and as supplementary fuel during the waste burn.

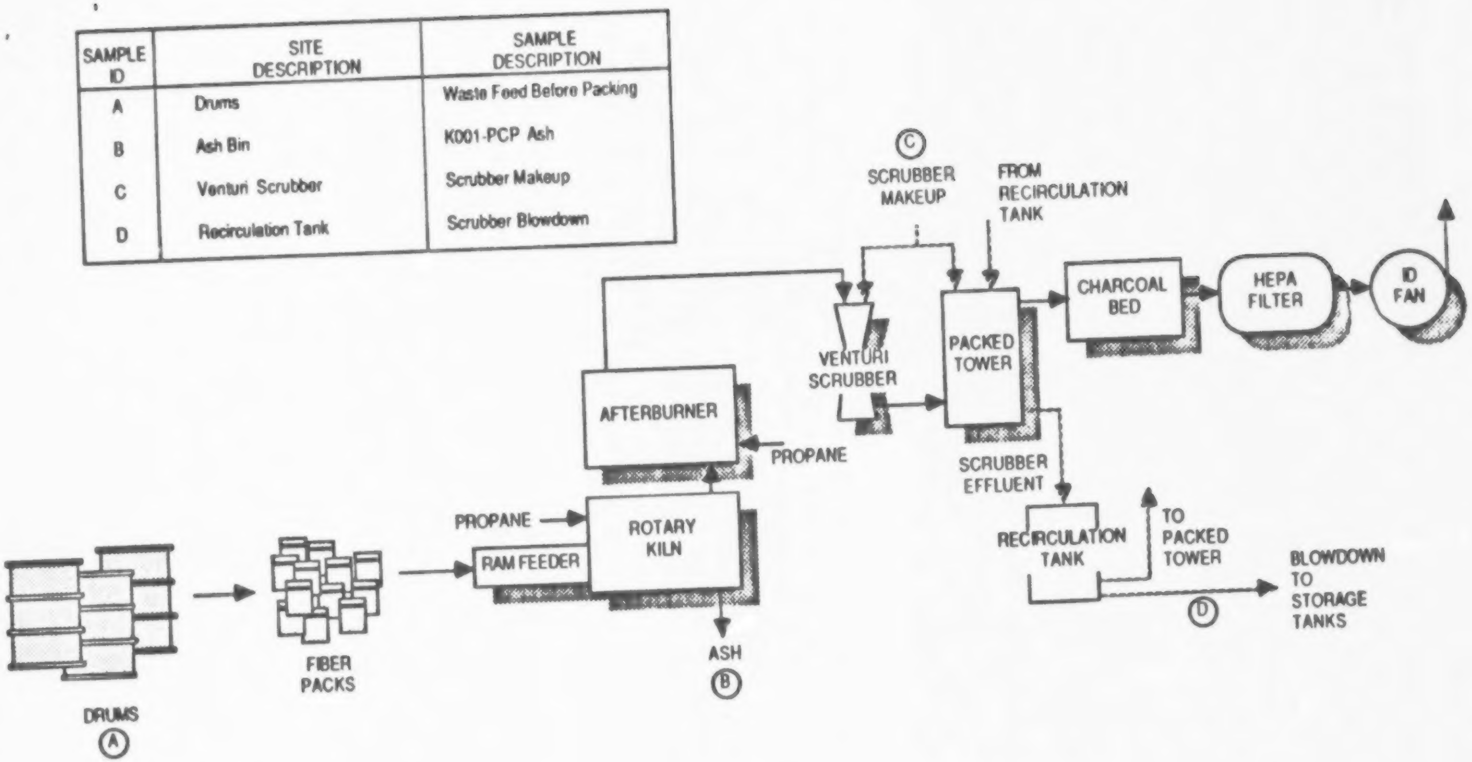
The hot combustion gases leaving the afterburner enter a venturi scrubber, which is followed by a packed tower, a carbon bed, and a high efficiency particulate air (HEPA) filter in series. An induced-draft (I.D.) fan is in line after the HEPA filter. The carbon bed and HEPA filter were added to the CRF system because of operating permit requirements.

Sodium hydroxide is added to the scrubbing system (venturi and packed tower) to maintain a pH greater than 7. Makeup water is added at a rate of 5 to 10 gallons per minute, and the water system is blown down continuously at a rate of 2.0 to 2.5 gallons per minute.

Strip charts continuously monitor and record oxygen (O_2), carbon monoxide (CO), and carbon dioxide (CO_2) at the afterburner outlet and after the scrubber system. An operator also manually recorded O_2, CO, CO_2, temperature, scrubber pressure drop, feed rate, and makeup and blowdown water flows every 15 minutes. U.S. EPA Modified Method 5 was used to collect pentachlorophenol samples in the stack gases after the scrubbing system but before the charcoal bed. EPA Method 8270 was used to measure concentrations.

The temperature in the kiln is controlled by increasing or decreasing waste feed rate, combustion air, and/or supplementary fuel. Waste feed rate was manually controlled by changing the rate of waste filled fiber packs fed to the incinerator. The feed rate was about 86 pounds per hour for the tests. Combustion air and supplementary fuel are also manually controlled by valve adjustments.

During the three tests, the rotary kiln operating temperatures ranged from about 1650° to 2000°F and afterburner temperatures ranged from about 1800° to 2100°F. Stack gas oxygen concentrations averaged about 6 percent with measured CO concentrations of less than 1 ppm to spikes exceeding 100 ppm.



DRUMS
Ⓐ
FIBER PACKS
PROPANE
RAM FEEDER
ROTARY KILN
ASH
Ⓑ
AFTERBURNER
PROPANE
VENTURI SCRUBBER
Ⓒ
SCRUBBER MAKEUP
FROM RECIRCULATION TANK
PACKED TOWER
SCRUBBER EFFLUENT
RECIRCULATION TANK
TO PACKED TOWER
Ⓓ
BLOWDOWN TO STORAGE TANKS
CHARCOAL BED
HEPA FILTER
ID FAN

SAMPLE ID	SITE DESCRIPTION	SAMPLE DESCRIPTION
A	Drums	Waste Feed Before Packing
B	Ash Bin	K001-PCP Ash
C	Venturi Scrubber	Scrubber Makeup
D	Recirculation Tank	Scrubber Blowdown

Figure 1. CRF rotary kiln incineration system and sampling points.

JOHN ZINK LIQUID INJECTION

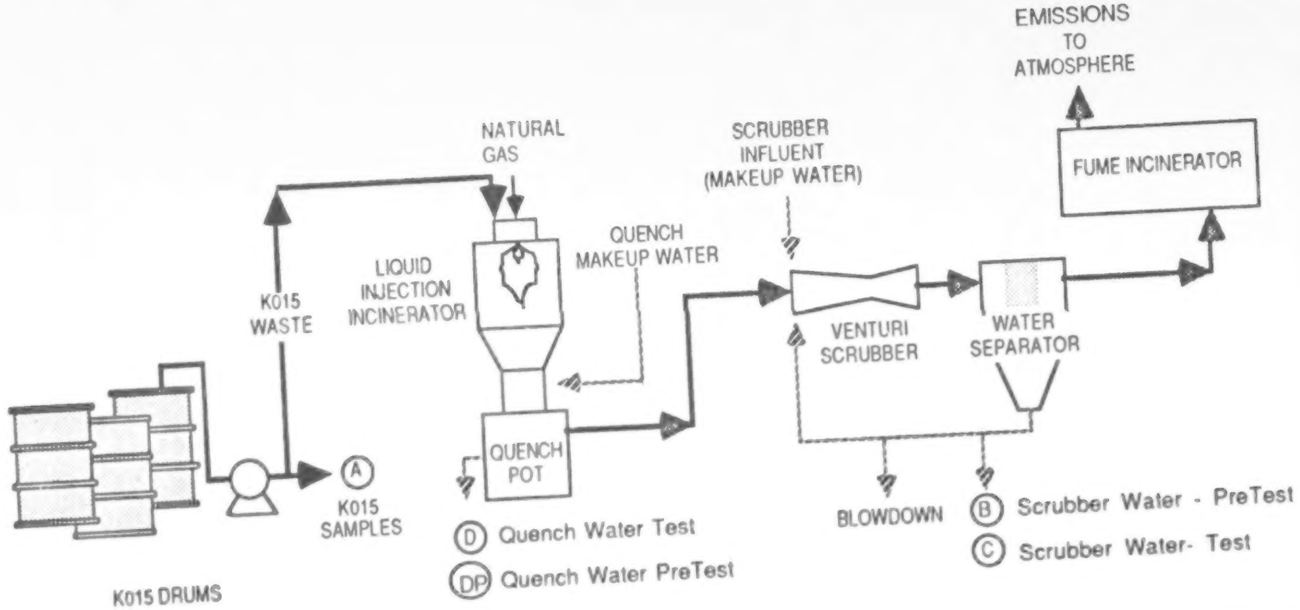
The John Zink incineration test facility, in Tulsa, Oklahoma, was used to conduct incineration tests of K015. The test facility used was a downflow (vertical) liquid injection unit with a minimum system input of 2 million Btu/hr and a maximum of 3 million Btu/hr (Figure 2). This unit provided a residence time of 2.5 seconds. Temperature was controlled by adding more combustion air or by injecting water or steam into the combustion chamber. The liquid injection unit has an inside diameter of 6 ft and a length of 6 ft. The incinerator was equipped with a John Zink High-Intensity Vortex^{R} burner.

Continuous monitoring and recording of CO_2, CO, O_2, and temperature were conducted in the exit zone of the thermal oxidizer unit at a point immediately prior to the quench pot sprays.

In addition, the Oklahoma State Department of Health (OSDH) required that a fume incinerator be used during all tests involving hazardous waste. This unit provided further thermal treatment of the primary combustion system's flue gas and was designed to operate at 2200°F with a residence time of 2 seconds.

The hot combustion gases leaving the primary combustion zone entered a quench zone, where contact water sprays cooled the gases. The quench pot water was treated with sodium carbonate to neutralize acid as it cooled the off-gas. The gases then entered an adjustable throat venturi scrubber, which was followed by a cyclonic flow knock-out chamber and a vent stack. Sodium carbonate also was added to the venturi scrubber water to provide final acid neutralization. The scrubber and the quench pot water systems were blown down as required to maintain solids levels in a 10 to 15 percent range. The liquid injection incineration system was equipped with multiple temperature-, pressure-, and flow-measuring devices that were monitored.

During the three tests, the incinerator operated at relatively constant conditions with combustion zone temperatures of about 2000°F and average K015 feed rates of 4.27 to 4.64 pounds per minute. Excess primary combustion air rates were maintained at 24 to 27 percent. The scrubber solution was maintained at a pH of 8 during Test 1, and between 6 and 7 during Tests 2 and 3. The pressure drop across the venturi scrubber was about 40 inches of water. The pH of the quench pot water was 6 to 7 during Test 1 and 7 to 8 during Tests 2 and 3.


EMISSIONS TO ATMOSPHERE
FUME INCINERATOR
NATURAL GAS
SCRUBBER INFLUENT (MAKEUP WATER)
QUENCH MAKEUP WATER
LIQUID INJECTION INCINERATOR
K015 WASTE
VENTURI SCRUBBER
WATER SEPARATOR
QUENCH POT
A
K015 SAMPLES
K015 DRUMS
BLOWDOWN
D Quench Water Test
DP Quench Water PreTest
B Scrubber Water - PreTest
C Scrubber Water- Test

SAMPLE ID	SITE DESCRIPTION	SAMPLE DESCRIPTION
A	Drums	Waste Feed
B	Venturi Scrubber Water	Scrubber Recycle Water -PreTest
C	Venturi Scrubber Water	Scrubber Blowdown
DP	Quench Pot Water	Quench Pot Water -PreTest
D	Quench Pot Water	Quench Pot Water - Test

Figure 2. The John Zink Company liquid injection incineration system and feed and residual sampling sites for K015.

SAMPLING AND ANALYSIS PROTOCOLS

K001-PCP TEST

The following four streams were sampled during the K001-PCP test burn:

Sampling Point	Description
A	K001-PCP waste feed
B	Rotary kiln ash
C	Scrubber makeup water
D	Scrubber blowdown

The process schematic diagram presented in Figure 1 shows the sampling points for the K001-PCP burn. A total of 1200 lb of waste was consumed in the test.

Table 1 presents the compounds targeted for each sample. Samples were prepared and analyzed in accordance with SW-846, 3rd edition. Ash samples were prepared using TCLP. To optimize quantitation for PCP, a slightly modified EPA Method 8040 (SW-846) was used for PCP extraction (an isothermal column oven was maintained at 170°C) and analysis (electron capture detector).

Pentachlorophenol was selected as the principal organic hazardous constituent (POHC) for stack sampling. The stack sampling point was between the scrubber-packed tower and the charcoal bed.

K015 TEST

The following five streams were sampled during incineration tests of K015:

Sample Point	Description
A	K015 waste feed
B	Scrubber water recycle - Pretest
C	Scrubber water blowdown
DP	Quench pot water - pretest
D	Quench pot water

The sample points are also noted in Figure 2. A total of 1600 lb of K015 was used in the three tests. No ash was generated during this test. Samples of K015 feed, scrubber water, and quench pot water were analyzed for volatile and semivolatile organics and purgeable and nonpurgeable organic carbon. The waters were also analyzed for metals. Specific compounds quantified are identified in Table 1.

The POHC's for this test were benzyl chloride and benzal chloride. The stack sampling point was between the water separator and the fume incinerator (Figure 2).

TABLE 1. CONSTITUENTS ANALYZED

Parameter	CAS no.
VOLATILES	
Acetonitrile	75-05-8
Acrolein	107-02-8
Acrylonitrile	107-13-1
Benzene	71-43-2
Bromodichloromethane	75-27-4
Bromomethane	74-83-9
Carbon tetrachloride	56-23-5
Carbon disulfide	75-15-0
Chlorobenzene	108-90-7
2-Chloro-1,3-butadiene	126-99-8
Chlorodibromomethane	124-48-1
Chloroethane	75-00-3
2-chloroethyl vinyl ether	110-75-8
Chloroform	67-66-3
Chloromethane	74-87-3
3-Chloropropene	107-05-1
1,2-Dibromo-3-chloropropene	96-12-8
1,2-Dibromoethane	106-93-4
Dibromomethane	74-95-3
Trans-1,4-Dichloro-2-butene	110-57-6
Dichlorodifluoromethane	75-71-8
1,1-Dichloroethane	75-35-3
1,2-Dichloroethane	107-06-2
1,1-Dichloroethylene	75-35-4
Trans-1,2-Dichloroethene	156-60-5
1,2-dichloropropane	78-87-5
Trans-1,3-Dichloropropene	10061-02-6
Cis-1,3-Dichloropropene	10061-01-5
1,4-Dioxane	123-91-1
Ethyl cyanide	10712-0
Ethyl methacrylate	97-63-2
Iodomethane	74-88-4
Isobutyl alcohol	78-83-1
Methyl ethyl ketone	78-93-3
Methyl methacrylate	80-62-6
Methyl methanesulfonate	66-27-3
Methylacrylonitrile	126-98-7
Methylene chloride	75-09-2
Pyridine	110-86-1
1,1,1,2-Tetrachloroethane	630-20-6
1,1,2,2-Tetrachloroethane	79-34-5
Tetrachloroethene	127-18-4
Toluene	108-88-3
Tribromomethane	75-25-2
1,1,1-Trichloroethane	71-55-6
1,1,2-Trichloroethane	79-00-5
Trichloroethene	79-01-6
Trichloromonofluoromethane	75-69-4
1,2,3-Trichloropropane	96-18-4
Vinyl chloride	75-01-4

Parameter	CAS no.
SEMIVOLATILES	
Acenaphthalene	208-96-8
Acenaphthene	83-32-9
Acetophenone	98-86-2
2-Acetylaminofluorene	53-96-3
4-Aminobiphenyl	92-67-1
Aniline	62-53-3
Anthracene	120-12-7
Aramite	140-57-8
Benz(a)anthracene	56-55-3
Benzenethiol	108-98-5
Benzidine	92-87-5
Benzo(a)pyrene	50-32-8
Benzo(b)fluoranthene	205-99-2
Benzo(ghi)perylene	191-24-2
Benzo(k)fluoranthene	207-08-9
p-Benzoquinone	106-51-4
Bis(2-choroethoxy)ethane	111-91-1
Bis(2-choroethyl)ether	111-44-4
Bis(2-choroisopropyl)ether	39638-32-9
Bis(2-ethylhexyl)phthalate	117-81-7
4-Bromophenyl phenyl ether	101-55-3
Butyl benzyl phthalate	85-68-7
2-sec-Butyl-4,6-dinitrophenol	88-85-7
p-Chloroaniline	106-47-8
Chlorobenzilate	510-15-6
p-Chloro-m-cresol	59-50-7
2-Chloronaphthalene	91-58-7
2-Chlorophenol	95-57-8
3-Chloropropionitrile	54-27-67
Chrysene	218-01-9
ortho-Cresol	95-48-7
para-Cresol	106-44-5
Dibenz(a,h)anthracene	53-70-3
Dibenzo(a,e)pyrene	192-65-4
Dibenzo(a,i)pyrene	189-55-9
m-Dichlorobenzene	541-73-1
o-Dichlorobenzene	95-50-1
p-Dichlorobenzene	106-46-7
3,3'-Dichlorobenzidine	91-94-1
2,4-Dichlorophenol	120-83-2
2,6-Dichlorophenol	87-65-0
Diethyl phthalate	84-66-2
3,3'-Dimethoxybenzidine	119-90-4
p-Dimethylaminoazobenzene	60-11-7
3,3'-Dimethylbenzidine	119-93-7
2,4-Dimethylphenol	105-67-9
Dimethyl phthalate	131-11-3
Di-n-butylphthalate	84-74-2
1,4-Dinitrobenzene	100-25-4
4,6-Dinitro-o-cresol	534-52-1
2,4-Dinitrophenol	51-28-5
2,4-Dinitrotoluene	121-14-2

Parameter	CAS no.
2,6-Dinitrotoluene	606-20-2
Di-n-octyl phthalate	117-84-0
Di-n-propylnitrosamine	621-64-7
Diphenylamine/ Diphenylnitrosamene	122-39-4/ 86-30-6
1,2-Diphenylhydrazine	122-66-7
Fluoranthene	206-44-0
Fluorene	86-73-7
Hexachlorobenzene	118-74-1
Hexachlorobutadiene	87-68-3
Hexachlorocyclopentadiene	77-47-4
Hexachloroethane	67-72-1
Hexachlorophene	70-30-4
Hexachloropropene	1888-71-7
Ideno(1,2,3-cd)pyrene	193-39-5
Isosafrole	120-58-1
Methapyrilene	91-80-5
3-Methylcholanthrene	56-49-5
4,4'-Methylenebis(2-chloroaniline)	101-14-4
Naphthalene	91-20-3
1,4-Naphthoquinone	130-15-4
1-Naphthylamine	134-32-7
2-Naphthylamine	91-59-8
p-Nitroaniline	100-01-6
Nitrobenzene	98-95-3
4-Nitrophenol	100-02-7
N-Nitrosodi-n-butylamine	924-16-3
N-Nitrosodiethylamine	55-18-5
N-Nitrosodimethylamine	62-75-9
N-Nitrosomethylethylamine	10595-95-6
N-Nitrosomorpholine	59-89-2
N-Nitrosopiperidine	100-75-4
n-Nitrosopyrrolidine	930-55-2
5-Nitro-o-toluidine	99-55-8
Pentachlorobenzene	608-93-5
Pentachloroethane	76-01-7
Pentachloronitrobenzene	82-68-8
Pentachlorophenol	87-86-5
Phenacetin	62-44-2
Phenanthrene	85-01-8
Phenol	108-95-2
2-Picoline	109-06-8
Pronamide	23950-58-5
Pyrene	129-00-0
Resorcinol	108-46-3
Safrole	94-59-7
1,2,4,5-Tetrachlorobenzene	95-94-3
2,3,4,6-Tetrachlorphenol	58-90-2
1,2,4-Trichlorobenzene	120-82-1
2,4,5-Trichlorophenol	95-95-4
2,4,6-Trichlorophenol	88-06-2
Tris(2,3-dibromopropyl)phosphate	126-72-7

Parameter	CAS no.
METALS	
Antimony	7440-36-0
Arsenic	7440-38-2
Barium	7440-39-3
Beryllium	7440-41-7
Cadmium	7440-43-9
Chromium	7440-47-3
Copper	7440-50-8
Lead	7439-92-1
Mercury	7439-97-6
Nickel	7440-02-0
Selenium	7782-49-2
Silver	7440-22-4
Thallium	7440-28-0
Vanadium	7440-62-2
Zinc	7440-66-6
DIOXINS AND FURANS	
Hexachlorodibenzo-p-dioxins	
Hexachlorodibenzofuran	
Pentachlorodibenzo-p-dioxins	
Pentachlorodibenzofuran	
Tetrachlorodibenzo-p-dioxins	
Tetrachlorodibenzofuran	
2,3,7,8-Tetrachlorodibenzo-p-dioxin	

TEST DATA

K001-PCP TEST DATA

Four samples of untreated K001-PCP, three samples of incinerator ash, and three samples of scrubber blowdown were taken and analyzed. Xylenes and toluene were found in the feed at 73 to 110 µg/g and 14 to 32 µg/g, respectively. The K001-PCP feed samples also contained polynuclear aromatic hydrocarbons (e.g., anthracene, fluoranthene, and naphthalene) ranging up to 50,000 µg/g (ppm). Pentachlorophenol concentrations in the feed ranged from 920 to 3000 ppm.

Methylene chloride was detected in one scrubber effluent sample at 61 µg/liter (ppb). No PCP or other semivolatile compounds were detected in any of the scrubber effluent/influent or ash samples.

The metals analysis showed zinc as the major metal present in these samples. Zinc ranged from 30 to 64 ppm in the feed and up to 11 ppm in the ash. Barium in the feed ranged from 17 to 30 ppm and concentrations were up to 74 ppm in the ash. Only barium (up to 0.32 ppm), lead (0.02 ppm in one sample), and zinc (0.03 ppm in one sample) were detected in the ash Toxicity Characteristic Leaching Procedure (TCLP) extracts.

No target dioxin/furan analytes were detected in any of the scrubber effluent/influent, waste feed, or ash samples.

Stack gas data are not currently available.

K015 TEST DATA

Six samples of untreated K015, three samples of quench pot water and three samples of scrubber water were taken and analyzed. Emission tests were conducted to determine the DRE.

The K015 feed used in the test burns consisted almost entirely of benzal chloride (88 to 100%). Benzyl chloride (3500 to 6400 µg/g) and benzotrichloride (3700 to 4500 µg/g) were also present. No other semivolatile organics were detected. This finding is consistent with information supplied by the generator. No toluene or other volatile organics were detected except for the following minor constituents in one sample of untreated K015:

Chloromethane (6.0 µg/g)
1,1,1,2-Tetrachloroethane (2.1 µg/g)
Tetrachloroethene (2.6 µg/g)

Toluene concentrations [15 to 59 parts per billion (ppb)] were detected in each of the three samples of quench water taken during the incineration tests. Each sample of quench water was found to contain anthracene (14 to 210 ppb), 2,4-dinitrophenol (15 to 44 ppb), phenanthrene (17 to 110 ppb), and phenol (12 to 21 ppb). Two samples also contained benzal chloride (66 and 94 ppb), and one contained benzotrichloride (16 ppb). The quench water also contained several trace metals. Chromium was found in the range of 4 to 34 parts per million (ppm); nickel, in the range of 2 to 25 ppm; and copper, in the range of 0.6 to 3.5 ppm. Other metals were present in lower concentrations. No volatile or semivolatile compounds attributable to incineration of K015 were detected in the scrubber water.

An emission test indicated a particulate rate of 1.689 lb/h at a concentration of 0.348 gr/dscf (equivalent to 0.311 gr/dscf at 7 percent oxygen). Much of this particulate (approximately 62 percent) was found to be sodium chloride, apparently formed in the scrubber from the interaction of sodium ions from the sodium carbonate and chloride ions from the HCl in the combustion gases. Trace metals were present in the particulate. Chromium, estimated at 0.03 percent of the particulate, was the major trace element found.

Hydrogen chloride emissions, determined during one test, were less than 0.9 ppm and the removal was greater than 99 percent.

The designated principal hazardous organic compounds (POHC's), i.e., benzal chloride and benzyl chloride, were found in the stack gas stream. The destruction and removal efficiencies for benzal chloride and benzyl chloride averaged 99.990 and 99.917 percent, respectively, based on two tests. Chlorobenzene was also found in the stack gas, but was below the detectable limit in the feed (less than 10 ppm); therefore, no DRE calculation was made.

Carbon monoxide emissions were generally quite low (less than 10 ppm) except for a few spikes (less than 1 minute in duration) when concentrations exceeded 500 ppm.

CONCLUSIONS

Incineration appears to be an effective method for treatment of both K015 and K001-PCP as indicated by the two tests. The residual ash and scrubber water samples contained only trace concentrations of organic or inorganic compounds. The excessive particulate emissions encountered during the K015 test could be reduced with a more effective air pollution control device. The low levels of volatile and semivolatile organics present in the K001-PCP and K015 scrubber waters may be related to the amount of wastes processed because somewhat higher organics were found in the tests of commercial incinerator air pollution control device effluents. The relatively low concentration of benzyl chloride in the feed, compared with the concentration of benzal chloride, affected the accuracy of the feed input rate for this compound and thus decreased the accuracy of the DRE determination.

ASSESSMENT OF VOLATILE ORGANIC AIR EMISSIONS FROM AN INDUSTRIAL AERATED WASTEWATER TREATMENT TANK

by: Bart Eklund
Radian Corporation
Austin, Texas 78720-1088

David Green
Research Triangle Institute
Research Triangle Park, North Carolina 27709

Dr. Benjamin Blaney and Lisa Brown
U. S. Environmental Protection Agency
Cincinnati, Ohio 45268

ABSTRACT

Volatile organics (VOs) may be effectively removed from wastewater prior to discharge by treatment in activated sludge systems containing aeration tanks. The relative contributions of air stripping/volatilization, biological oxidation, and solids sorption to total disappearance of VOs in such systems have not been extensively characterized. Studies were conducted at a full-scale treatment facility to determine the relative extent to which specific compounds are lost to the atmosphere. Direct measurements of air emissions were made via collection and chemical analysis of off-gases from an aerated tank of an activated sludge unit. Multiple air emission measurements were made to determine the total off-gas flow rate, the emission rate of specific compounds, and the associated spatial variabilities. The emissions were compared to the overall volatile organics losses as determined from analysis of influent and effluent liquid streams. This paper describes these measurement techniques and the results of the study.

INTRODUCTION

The U.S. Environmental Protection Agency (EPA), through its Hazardous Waste Engineering Research Laboratory (HWERL) and other offices, conducts projects in support of the U.S. EPA implementation of PL 94-580, "The Resource Conservation and Recovery Act" and the 1984 Amendments. To adequately protect human health and the environment, regulations are being considered for air emissions from aerated and quiescent surface impoundments, tanks, and basins. Emissions from quiescent impoundments have been characterized to a limited extent, while those from aerated units have been studied less. In both cases, there is limited information available to determine the magnitude of emissions from these processes or to model those emissions.

Industrial wastewater treatment (WWT) systems typically include surface or subsurface aeration units with an active bioculture to remove dissolved organic compounds prior to discharge or reuse of the water. Aerobic organisms can use certain organic compounds in dilute concentrations as a food source. For maximum cost effectiveness, oxygen must be supplied to these organisms by bubbling air through the wastewater and/or agitating the surface of the wastewater. A large mass of the aerobic organisms is necessary to achieve high removal rates, so the biomass, or activated sludge, is normally allowed to recycle and build up to a concentrated level. Besides providing oxygen, the aeration system acts to keep this biomass in suspension and provides mixing.

Wastewater typically requires several hours of residence time within the aeration unit for the biological oxidation of the dissolved organic compounds to near completion. If volatile organics (VOs) or semivolatile organic compounds are present in the wastewater, then these compounds may also be removed via mass transfer to the atmosphere. A third potential pathway for organic compound removal is via sorption onto the biomass and ultimate disposal in the wasted solids. The relative contributions of air stripping/volatilization, biological oxidation, and solids sorption to total disappearance of VOs in aerated, activated sludge systems have not been extensively characterized. This paper describes a study conducted at a full-scale treatment facility to determine the relative extent to which specific compounds are lost to the atmosphere. Radian Corporation and Research Triangle Institute (RTI) jointly performed the field work during August 1987.

DESCRIPTION OF THE TEST SITE

The test site was located at a large petroleum refinery which produces fuels and chemicals. The site was chosen because its subsurface aeration pattern appeared to be uniform, and because several volatile compounds were present at levels over 100 ppb at the influent to the aeration tank. The wastewater treatment plant treats an average of 23 to 26 million liters of wastewater per day, primarily from continuous processes. Two separate process streams are present. The wastewater first goes to skim and surge tanks, followed by API separators. One process stream then empties directly to the oxidation tanks, while the second process stream is further treated in another separator, roughing filters, and primary clarifiers before entering the oxidation tanks. The wastewater is split between two oxidation tanks, is recombined, then split again between two final clarifiers, before finally being filtered and discharged to a nearby river. Sludge is recycled from the clarifiers back to the oxidation tanks.

One of the two identical oxidation (aeration) tanks was studied. Each tank is 36.6 m in diameter, 5.5 m deep, and has a capacity of 5.7 million liters. Typical flow through the system is 19,000 to 23,000 liters per minute. The wastewater retention time in the oxidation tanks is typically 8 hours, and the total retention time upstream of the oxidation tanks is about one day.

Oxidation air from a 260 cubic meters per minute (9,250 cfm) capacity compressor is split evenly to the two oxidation tanks. The air enters the tanks through dispersion rings located near the tank bottom that have 2,000 diffusers per tank. The dissolved oxygen in the tanks is monitored and maintained above 1 mg/L. The biological oxygen demand (BOD) removal is routinely monitored. The influent values are usually 25-100 mg/L, but may reach 200 mg/L. The effluent BOD is typically 1-2 mg/L.

EXPERIMENTAL APPROACH

The sampling strategy, sampling techniques, and analytical methods are summarized below. Further detail is available in the project reports (1,2).

Sampling Strategy

The oxidation tank was divided into five concentric circles, each having an equal area. Emissions from the tank were measured along a transect line at the midpoint of each ring. In addition to these ten points, the tank's centroid and three other points were also sampled as shown in Figure 1. The three additional sampling points were selected to coincide with the aeration rings. Seven sampling points (2, 5, 7, 10, 12, 13, and 14) were directly over the aeration rings. The seven remaining sampling points (1, 3, 4, 6, 8, 9, and 11) were relatively quiescent.

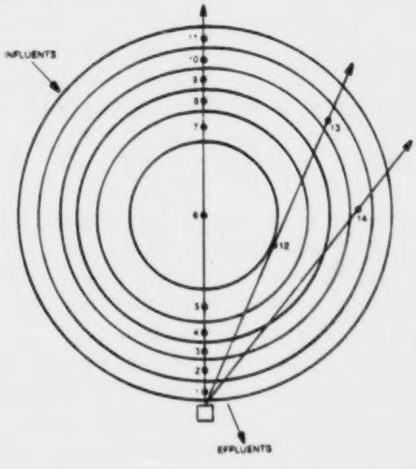


Figure 1. Depiction of sampling locations for oxidation tank.

An enclosure device, the isolation emission flux chamber, was used to measure the off-gas flow rate and to collect samples of the emitted gas. Off-gas rate measurements and VO emission rate measurements were made concurrently. The total air flow to the oxidation tank was estimated from the vendor's fan curve.

The first day of sampling was used to assess the radial spatial variability of the tank emissions in terms of VO emissions and air flow rate. To accomplish this, flow rate measurements and total non-methane hydrocarbons (TNMHC) concentration measurements were made at seven points along the transect line of the tank. Only on-site analytical data were developed. Based upon this preliminary work, the tank was determined to contain no separate distinct radial zones of emissions, i.e., emissions were homogeneous.

The second and third sampling days were used to characterize the emissions of the oxidation tank. Gas samples were collected for on-site analysis of methane and TNMHC, and a gas sample for off-site detailed speciation was collected at each sample point. A total of twelve points were sampled, with three points repeated. Liquid grab samples and composites were collected from the influent and effluent streams to the oxidation tank.

Sampling Procedures

The chosen air sampling approach used an enclosure device, referred to as an emission isolation flux chamber, to sample gaseous emissions from a defined surface area. This approach has previously been used for measuring VO emission rates from aerated (3) and quiescent (4) surface impoundments, as well as solid emission sources (4,5). Normally, clean, dry sweep air is added to the chamber at a fixed, controlled rate. For this site, the diffused aerator provided sufficient air flow to the flux chamber, so no additional sweep air was needed. A pump was used to withdraw sample gas from the flux chamber at the same rate it entered the aerators as indicated by the chamber pressure. The air flow rate was adjusted until the average chamber pressure, as measured by a water manometer, was zero. The volumetric flow rate of air through the chamber was manually recorded from visual readings of a rotameter float. Gas samples were collected at the exit of the chamber. The emission rate was calculated as:

$$E.R._i = \frac{(C_i)(Q)}{A}$$

where: $E.R._i$ = emission rate of species, i (ug/m^2min);
C_i = measured concentration of species i (ppmv converted to ug/m^3);
Q = air flow rate (m^3/min); and
A = exposed surface area (m^2).

The flux chamber used was a flat-topped acrylic cylinder that enclosed an area of 0.29 m^2 and had an internal volume of 0.130 m^3 assuming a 2.5 cm depth of penetration. Four 0.6 cm (1/4 inch) ports were used to withdraw the off-gas. Other ports were used to measure the temperature inside the chamber and the internal pressure.

The sample gas stream passed through a calibrated rotameter with a precision flow controller. A console was constructed with three rotameters capable of monitoring a range of off-gas rates from 0 to 80 L/min. All components in contact with the gas were glass, teflon, or stainless steel. A sampling manifold was used for gas sample collection. Samples for on-site analyses were collected in precision lock, 100 mL teflon and glass syringes. The samples were shielded from direct sunlight and analyzed within one hour of collection. Gas samples for off-site analyses were collected in evacuated, 2.8 liter Summa polished, stainless steel canisters.

A variety of procedures was used to collect liquid samples. Grab samples of influent streams were collected from existing valves, and effluent samples were bailed from the tank at an overflow weir using a teflon bailer. All grab samples were collected in 40 mL zero headspace septum vials, preserved with HCl to a pH below 2, and refrigerated until the time of analysis. Composite samples of the influent, recycle influent, and effluent were collected over a six-hour or longer period using a syringe pump that gradually filled two 50 mL syringes from a slipstream of the process water. The entire sampling apparatus was cooled throughout the sampling period. When full, the syringes were decanted into acidified 40 mL septum vials.

Analytical Procedures

The on-site analyses were used to provide feedback to assess the sampling strategy. They were limited to gas-phase analyses of the air samples collected in gas-tight syringes from the outlet of the flux chambers. A Shimadzu Mini-2 gas chromatograph (GC) with a flame ionization detector was used to determine the concentrations of total non-methane hydrocarbons (TNMHC) and methane (CH_4) in the effluent air samples from the flux chamber.

The off-site analyses included the chemical speciation of the flux chamber air samples collected in stainless steel canisters and chemical speciation of the various liquid samples. Additional sampling and analyses were performed that are not addressed in this paper.

Chemical speciation of the air and some selected liquid samples for C_2 to C_{12} hydrocarbons was performed with a Varian 3700 gas chromatograph fitted with a flame ionization detector and a photoionization detector. The chemical species were cryogenically concentrated to increase the sensitivity of the analyses. Liquid samples were analyzed using a purge-and-trap technique modified to utilize the cryogenic trap. For both air and liquid samples, total volatile organics concentrations were obtained as the sum of the species concentrations.

Grab samples from the influent and effluent streams were analyzed for benzene, toluene, and xylenes (BTX) by EPA Method 602. The EPA Method 602 results were confirmed by mass spectroscopy using EPA Method 624. A composite of the oxidation tank influent was analyzed for extractable organic priority pollutants by EPA Method 625 to establish the background of organics present in the wastewater. Finally, the volatile suspended solids content of recycle and effluent sample splits were determined by Standard Method Number 209E.

SAMPLING AND ANALYSIS RESULTS

Fifteen off-gas rate measurements and thirteen emission rate measurements were made at the oxidation tank. The results of these measurements are summarized in Table 1. The experimental coefficients of variability were 34.4% and 62.9% for the off-gas and TNMHC measurements, respectively.

TABLE 1. SUMMARY OF FINDINGS FROM OFF-GAS AND EMISSION RATE MEASUREMENTS

Measurement	Weighted Average	Total
Off-Gas Rate ($m^3/min\cdot m^2$)	0.119	--
TNMHC[*] Emission Rate ($ug/m^2\cdot min$)	2410	--
TNMHC[*] Emissions (ug/min)[#]	--	2,530,000
Methane Emission Rate ($ug/m^2\cdot min$)	1,050	--
Methane Emissions (ug/min)[#]	--	1,110,000

[*] Total non-methane hydrocarbons (excluding oxygenated species).
[#] Surface area = 1050 m^2.

The total air emissions for the major individual compounds that were detected are given in Table 2. Methane and straight-chain aliphatic compounds account for the majority of the emissions. The total non-methane hydrocarbon emission rate corresponds to a daily emission of less than 4 kg.

TABLE 2. TOTAL EMISSIONS FOR SELECTED INDIVIDUAL COMPOUNDS

Compound	Average Emission Rate (ug/m^2-min)	Total Emissions (mg/min)
Methane	1054	1106
C-3 VOC	35.1	36.8
n-Heptane	58.2	61.1
n-Octane	110	116
n-Nonane	144	151
n-Decane	124	130
n-Undecane	73.1	76.8
3-Methylheptane	47.3	49.7
Methyl-cyclohexane	40.9	43.0
Toluene	52.5	55.1
Cyclopentane	5.74	6.03
Isoheptane	26.4	27.7
Benzene	5.20	5.46
p,m-Xylene	11.8	12.4
o-Xylene	8.96	9.41
Ethylbenzene	3.03	3.18
TNMHC	2410	2530

The average measured air flow converts to 125 m^3/min of off-gassing from the entire tank. The spatial variability in the off-gas rate was ±12%, but the accuracy of the sampling technique has not been assessed. A total air flow of 141 m^3/min was estimated from the fan curve for the compressor in service. The measured value is 11% less than this estimate.

The average concentrations of selected species in the influent and effluent streams of the tank are given in Table 3. The total mass of individual compounds entering the oxidation tank was determined by multiplying the average concentration in the wastewater by the average flow rate for each of the three influent streams for the time period when air sampling was conducted. These data are shown in Table 4. The liquid concentration data were from the 2-3 samples per influent stream analyzed using the Varian GC. The estimated percentage of each compound that was volatilized is also shown. The values agree well with other published data for aromatic compounds (6).

TABLE 3. AVERAGE LIQUID-PHASE CONCENTRATIONS FOR WASTEWATER STREAMS

Compound	4F Influent Stream (ug/L)	2B Influent Stream (ug/L)	Recycle Influent Stream (ug/L)	Effluent from Tank* (ug/L)
Benzene	440	9.67	0.21	BDL#
Toluene	274	19.0	0.26	BDL#
m,p-Xylene	466	49.1	0.42	BDL#
o-Xylene	209	25.1	0.35	BDL#
n-Nonane	122	11.5	0.94	---
n-Decane	105	23.4	BDL	BDL†
n-Undecane	107	24.2	0.58	BDL†
Methylcyclohexane	114	BDL	0.26	---
TNMHC	5,010	663	41.0	---

*Effluent was analyzed using a separate analytical protocol and analytical system.
#BDL = below detection limit (0.3-3.8 ug/L).
†Detection limit = 10 ug/L.

TABLE 4. INFLUENT WASTEWATER MASS LOADINGS AND ESTIMATED VOLATILE LOSSES

Compound	Total Mass Loading of Influent Wastewater (g/min)	Estimated Volatile Losses (% of Influent Conc.)
Benzene	2.50	0.2
Toluene	1.59	3.5
p,m-Xylene	2.76	0.4
o-Xylene	1.24	0.8
n-Nonane	0.72	21
n-Decane	0.66	20
n-Undecane	0.68	11
Methylcyclohexane	0.64	6.7
TNMHC	30.1	8.4

The analysis of the influent streams to the oxidation tank indicated that the recycle sludge had negligible VOs (i.e., no loss of VOs via sorption to the biomass). Likewise, the effluent liquid from the tank had no detectable BTX; indicating that essentially complete removal of these compounds occurred in the oxidation tank.

CONCLUSIONS

The tank was found to contain a single zone of emissions (i.e., no clear trends in spatial variability were determined). Overall, the air emissions from the tank were low, both on an absolute basis and as a percentage of the influent VOs. The ratio of methane to TNMHC emissions was about 1:2. The source of the methane has not been determined, though an anaerobic layer at the bottom of the tank is one possibility. Relatively large methane emissions have also been measured at another aerated tank (3). The flux chamber sampling method exhibited good precision and appears to be accurate based on comparisons of total air flow to fan curve data.

NOTICE

The information in this document has been funded wholly or in part by the U. S. EPA under contract to Radian Corporation and Research Triangle Institute. It has been subject to the Agency's peer and administrative review, and it has been approved for publication. Mention of tradenames or commercial products does not constitute an endorsement or recommendation for use.

REFERENCES

1. Eklund, B., et al. Results of Radian's air emission measurement at plant A3's wastewater treatment system. Draft Report to U. S. EPA/HWERL, October 9, 1987.

2. Green, D. Field assessment of air emissions from an industrial wastewater treatment system at plant A-3. Draft Report to U.S. EPA/HWERL, February 18, 1988.

3. Green, D. and B. Eklund. Field assessment of the fate of organics in aerated waste treatment systems. Paper presented at the 13th Annual EPA Symposium on Land Disposal, Remedial Action, Incineration and Treatment of Hazardous Waste, May 1987.

4. Eklund, B. M., W. D. Balfour, and C. E. Schmidt. Measurement of fugitive volatile organic emission rate. Environmental Progress, 4: 3, 1985.

5. Wetherold, R. G., B. M. Eklund, B. L. Blaney, and S. A. Thornloe. Assessment of volatile organic emissions from a petroleum refinery landtreatment site. Paper presented at the Hazardous Materials Control Research Institute's 3rd National Conference on Hazardous Wastes and Hazardous Materials, March 1986.

6. Namkung, E. and B. E. Rittmann. Estimating VOC emissions from publicly owned treatment work. Journal WPCF, 59: 7, July 1987.

CALIFORNIA DEPARTMENT OF HEALTH SERVICES/EPA STATUS UPDATE OF THE CALIFORNIA LAND DISPOSAL RESTRICTIONS AND IMPACT/IMPLEMENTATION PROGRAM

Robert Ludwig and Benjamin Fries
California Department of Health Services
Sacramento, CA 95814

ABSTRACT

The California Department of Health Services (DHS), in cooperation with the U.S. EPA, is conducting demonstrations of alternative treatment technologies and studies on hazardous waste management. The overall objective of the California Waste Management Program is to reduce the amount and eventually eliminate land disposal of untreated hazardous wastes. Strategies being studied include source reduction, recycling, and treatment.

This paper provides an update of EPA-funded projects illustrating California's Waste Reduction Program. Specific studies include: 1) Research, Development, and Demonstration Projects (RD&D); 2) Waste Management Information Transfer; 3) Metal Finishing Waste Audit; 4) Waste Stream Information Accumulation and Analysis; and 5) Source Reduction Resource Partnership.

BACKGROUND

In December, 1982, California's Land Disposal Restrictions Program was initiated by DHS which implemented a regulatory program to phase out land disposal of specific hazardous wastes. This program provided a schedule of land disposal restrictions for certain hazardous wastes, the California List, which includes liquids with high levels of cyanides, metals, PCB's, halogenated organic compounds, or a pH of less than 2.

In order to assist and move industry towards alternatives to land disposal, DHS initiated the Waste Reduction Program in July, 1984. The various program elements are designed to provide technical assistance, information/technology transfer, economic and regulatory incentives.

Part of California's Waste Reduction Program has involved a Cooperative Agreement with the EPA entitled "California Land Disposal Restrictions Impact and Implementation Evaluation Program." This 3-year project started in December, 1985, has provided DHS with staff and contractual support to effectively evaluate new waste generation, reduction, recycling, treatment, and destruction technologies capable of processing hazardous wastes.

INTRODUCTION

The purpose of this paper is to provide a status update on the EPA-funded projects. Program areas include: 1) RD&D; 2) Waste Management Information Transfer; 3) Metal Finishing Waste Audit; 4) Waste Stream Information Accumulation Analysis; and 5) Source Reduction Research Partnership. A summary of these projects is presented in Table 1.

RESEARCH, DEMONSTRATION, AND DEVELOPMENT PROJECTS

The status of 4 RD&D projects for the treatment or on-site recycling of hazardous wastes is presented below.

Aerobic Composting System for Pesticide Rinsewaters

In December, 1987, California Agricultural Research set up an Aerobic Composting System at the Chemical Waste Management Inc. facility in Kettleman City, CA, to determine the feasibility of treating pesticide rinsewaters. Two 25-gallon additions of a Simizine/carbofuran-water mixture have been applied to the 14' x 5' x 30' compost system consisting of cotton gin wastes and chicken manure. A similar compost system receiving only water is serving as a control. Both compost systems are being maintained aerobically via a forced air perforated pipe network.

Preliminary results from the first application indicate a degradation of carbofuran from 50-1 mg/L over a 7 day period. Simizine degradation from 70-3 mg/L occurred over 40 days. Temperatures in the compost system ranged from 11-67^{o} with a mean and standard deviation of 48 $\pm$ 10^{o}, (n=40).

A second application of carbofuran/simizine was then added to the same treated compost pile. The pesticides did not degrade as quickly as the first application and the temperature in the system was considerably lower. Carbofuran degradation occurred from 87-50 mg/L after 21 days while simizine degraded after 21 days from 50-8 mg/L. Temperatures in the system ranged from 6-18^{o} C with a mean and standard deviation of 8 $\pm$ 6^{o} C, (n=21).

Chlorinated Solvent Adsorption Using Ambersorb XE-340

Woodward-Clyde Consultants are currently evaluating Ambersorb XE-340, a synthetic carbonaceous polymer as an alternative to activated carbon, for the removal of chlorinated solvents from contaminated groundwaters. In addition, an evaluation of adsorbent regeneration within the column utilizing steam will be performed.

Two resin columns (10 x 150 cm) containing 11 liters of Ambersorb XE-340 adsorbent, are being operated in parallel. The 2 contaminants in the feed water are trichloroethylene (TCE) at 10.7 ppm and 1,1,1-trichloroethane (TCA) at 0.58 ppm. Complete TCE

TABLE 1. SUMMARY OF CALIFORNIA'S WASTE REDUCTION PROGRAM

CONTRACTOR	PROGRAM AND WASTE TYPE	PROJECT	STATUS
Cal Ag Res. Dr. Michael Beevers	Biological treatment. Pesticide rinseates.	Application of pesticides to aerated compost system.	Research ongoing. Report due 8-88.
Woodward-Clyde. Mr. David Marrs	Physical separation. Adsorption on substrate. Aqueous solutions of organics.	Evaluation of Ambersorb XE-340 in columns for removal of organics, TCA and TCE.	Field work completed. Report available 8-88.
Dept. Env. Tox. UC, Davis. Dr. Wray Winterlin	UV/H_2O_2 oxidation. Aqueous waste, pesticide rinseates.	Evaluation of UV/H_2O_2 system for treatment of pesticides rinseates	Report available.
Ogden Products, Mr. William Rickman	Incineration, thermal reactor. Aluminum spent potlining wastes containing cyanides and fluorides.	Evaluation of spouted-bed combustor and additives to increase treatment efficiency.	Laboratory testing completed. Report available 8-88.

(Continued)

TABLE 1. SUMMARY OF CALIFORNIA'S WASTE REDUCTION PROGRAM

CONTRACTOR	PROGRAM AND WASTE TYPE	PROJECT	STATUS
Energy & Environmental Res. Mr. Pat Nelson	Oil waste management alternatives. Waste oils.	Demonstration & evaluation of oil re-refinery system and waste reduction alternatives.	Field work being completed. Report due 8-88.
PRC Environmental Management, Mr. Dominick DeRienzo	Waste Audit Study. Metal plating and finishing wastes.	Waste audit study for the metal finishing industry. Self-audit manual & report.	Data collection ongoing. Report due 8-88.
Alt. Tech. TSCD, CA. DHS, Mr. Robert Hosea	RCRA and California wastes.	Waste stream information collection & analysis of 1987 Biennial Generator & Annual Facility Reports.	Data collection & analysis in progress. Report due 10-88.
Source Reduction Research Partnership (SRRP), Dr. Katy Wolf	Source reduction options. Chlorinated solvents.	Quantification of halogenated solvent waste reduction of industries in 6 county area of LA.	Data collection in progress. Final report due 12-89.

saturation (inf. equaling eff. concentration) occurred after 7,000 bed volumes of water at a feed rate of 1.64 LPM (9.2 bed volumes/hour). The final TCE loading on the adsorbent was about 40% of the predicted equilibrium adsorption isotherm. Complete TCA saturation occurred after treatment of 4,500 bed volumes of water with the final TCA loading about 13% of the loading predicted by the equilibrium adsorption isotherm.

The first indication of TCA breakthrough (eff. greater than 0.01 ppm) occurred after 800-1,000 bed volumes at a feed rate of 0.44 L/minute (2.4 bed volumes/hour). It appears that TCE breakthrough was just about to begin after 1,200 bed volumes of water. It was estimated that complete TCA and TCE saturation would occur after an additional 4,000 bed volumes over a 3 month period. A flow rate of 1.65 LPM (5 GPM) was determined to be acceptable for future studies to provide an acceptable loading rate for TCE removal. Furthermore, there appeared little process advantage to a lower flow rate which would be too low for practical scale-up.

The next step of the study will involve the evaluation of a steam generator for the regeneration process of the Ambersorb XE-340 within the columns.

UV/Hydrogen Peroxide Treatment For Destruction of Pesticide Waste

The Dept. of Environmental Toxicology of UC Davis, has completed an evaluation of a small ultraviolet (UV) and oxidation system, Perox Pure Model SQ, manufactured by Peroxidation Systems, Inc., to treat a broad range of pesticides and study variables related to the treatment process[1]. Specific compounds and pesticides treated were m-xylene, Captan, Pentachloronitrobenzene (PCNB), and Propazine.

The unit has a reactor and a reservoir capacity of about 20 liters each. The reactor/oxidation chamber is a stainless steel cylinder (24" x 8.6") and receives UV light by an axially mounted high pressure mercury vapor lamp delivering radiation in the 190-400 nanometer range. For the majority of experiments, H_2O_2 and a proprietary catalyst were fed continuously into the reactor. Wastewater was circulated at 12 LPM through the system and returned to the holding reservoir. The residence time in the reactor was 1.67 minutes.

Some of the test results are presented in Table 2-Pesticide Degradation Utilizing a UV/H_2O_2 System. The unit rapidly degraded all of the compounds in optically clear water. It is important to note that the rates of breakdown of these compounds were not significantly dependent on the presence of H_2O_2 or the catalysts.

The m-xylene was used as a test chemical since xylenes are common components in emulsifiable concentrate pesticide formulations. Two different concentrations of m-xylene were degraded to about the same level after 37-45 minutes w/ or w/o H_2O_2 or catalyst. Due to the low water solubility of Captan, a carrier solvent (5% methanol v/v) was added to the system. Captan breakdown from 10-0.03 ppm occurred after 16 minutes w/ or w/o H_2O_2 or catalysts. Higher Captan concentrations of 60 and 125 ppm (using a commercially available wetable powder formulation which made a cloudy solution for the 125 ppm solution) resulted in final concentrations of 0.61 and 0.01 ppm after 30 and 89 minutes. The slower degradation rate of the latter solution may be caused by the cloudiness of the solution.

TABLE 2. PESTICIDE DEGRADATION UTILIZING A UV/H_2O_2 SYSTEM

Chemical	Initial Conc. (ppm)	H_2O_2 Conc. (ppm)	Catalyst	Final Conc. (ppm)	Time of Operation (minutes)
m-xylene	23	0	None	0.37	37
m-xylene	50	115	None	0.50	45
Captan	10	0	None	0.03	16
Captan	10	115	Yes	0.03	16
Captan	60	115	Yes	0.61	30
Captan WP*	125	115	None	0.01	89
PCNB	2	0	None	0.005	15
PCNB	2	115	Yes	0.005	28
Propazine	7	0	None	0.04	30
Propazine	12	115	None	0.03	30

* Captan in a wet powder formulation

Water solubility of PCNB is extremely low, 0.44 ppm, so most of the experiments were conducted at 2 ppm with a 5% solution of isopropanol as a carrier solvent. PCNB was rapidly degraded in clear water by the UV light without H_2O_2 or any catalysts. UV light only proved to be the best condition for the degradation of PCNB in aqueous and isopropanol solutions. PCNB broke down after 15.5 minutes from 2-0.01 ppm under these conditions.

Propazine also had low water solubility (3 ppm) but solutions of 7.4 & 12.6 ppm were generated using 5% isopropanol. H_2O_2 had no effect on the degradation rate of propazine and it took 30 minutes to degrade the 2 solutions to 0.04 ppm.

In conclusion, the unit was found to be applicable for treatment of low levels of pesticides and other pollutants in clear water was not shown to be effective use for degrading high concentrations in cloudy solutions.

Circulating Bed Combustion Of Spent Potliners

Ogden Environmental Services Inc., is conducting a series of 20 parametric combustion tests in a small-scale, 2-inch diameter spouted-bed combustor system to determine the effectiveness of additives in preventing the agglomeration of spent potliner types. Aluminum spent potliners (SPL) are a solid waste by-product of aluminum smelters that contain soluble species of cyanides and fluorides. Over 2 million tons of SPL are stockpiled in the U.S. awaiting development of an effective treatment technology.

This spouting bed combustor (SBC) constitutes an intermediate testing phase between muffle furnace and the pilot-plant circulating bed combustor (CBC) unit. The spouting bed unit will be used to study the fluidization and agglomeration behavior of potential waste feeds and to determine the performance of agglomeration-inhibiting additives during fluidized bed combustion of wastes with low melting temperatures. For the proposed series of tests, a test matrix was established with 1) SPL type; 2) additive type; 3) additive ratio; and 4) initial combustor temperature. Also, 1 test was varied by using sand instead of alumina as an inert bed material.

Tests showed that potliners produced by different aluminum manufacturers behaved differently in the SBC. The 3 additives produced agglomeration temperatures ranging from 825-900° with the 4 different SPL types. An additive ratio of 20% appeared to be the minimum, while a maximum of 40% increased the agglomeration temperature to 930° C.

Leachability tests were conducted on the ash samples for cyanide and fluoride. Cyanide levels were reduced from 2,000-0.76 and 0.06 mg/L, using the EPTOX and the California Waste Extraction Test. Fluoride leachability was effectively reduced several orders of magnitude by the addition of 15 wt percent $CaCl_2$ powder to the SPL ash. The resultant blend of 35 mg/L was below the levels required by the EPA and DHS.

Overall, the SPC test program demonstrated that several different types of additives can be used to control agglomeration, with distinct differences in resultant agglomeration temperatures. Potliners from different aluminum producers behaved differently, but agglomeration was controlled with sufficient quantities of additives.

WASTE MANAGEMENT INFORMATION TRANSFER

Oil Waste Management Alternatives Symposium

A report and symposium on oil waste management was completed by Energy and Environmental Research Corporation. The study and symposium seek to interest, encourage, and assist industries with improving their management of oil wastes. It identified effective alternatives that could lead to a reduction in oil generated and/or increase the recyclability of oil waste.

The report focused on alternatives that can be implemented by industry and recommendations that can be made by the DHS to generators. Types of oil wastes resulting from oil usage included lubricants, coolants, cutting and machining oils, and hydraulic fluids. PCB oil or oils from other major process residues resulting from petroleum refining, production of oil products, petrochemical manufacture, and other major process residues where oil is a raw material or a product were not included. The report and symposium also presented technological, economic, and regulatory aspects.

An in-depth discussion of a used oil re-refinery system was also presented. The system demonstrates hydro-refining technology at a full-scale production capacity. Hydro-refining is an established technology in crude oil refining, but has not been utilized in used oil re-refining. This information can establish whether the system has economic viability over an extended time period. It could possibly lead to wide-spread oil collection and hydro-refining as an ongoing waste management technology.

The results of the report were presented to industries, regulatory agencies, and environmental consultants, and the public at 2 two-day technical symposia in April, 1988. Total attendance was around 700 for the two seminars.

METAL FINISHING WASTE AUDIT PROJECT

A waste audit study for the metal finishing industry is now underway by PRC Environmental Management, Inc. The study will identify waste reduction technologies available to the industry and develop a waste reduction audit protocol that can be used by metal finishers to assess their own waste reduction opportunities.

To meet the objectives, PRC is performing waste audits at 3 small to medium sized metal finishing plants in the San Francisco Bay area. Initial visits have been conducted, background information is now being reviewed, and areas where waste reduction technologies may be implemented are being identified. A second visit will be conducted to fill in data gaps identified during the review of the background and to gain more detailed information about process requirements, work procedures, and hazardous waste generation.

PRC will then identify and evaluate the applicability of implementing various waste reduction technologies into the plant manufacturing processes. The costs of implementing these technologies will be compared with the potential savings in waste reduction. The findings of each audit will be summarized in a report and submitted to each plant. After review by plant personnel, a third visit will be made to meet and discuss management's reactions to findings and recommendations of the audit. At that time, PRC will find out if the company is planning on implementing the recommendations made in the report and if not, why such a decision was made.

After completion of individual waste audits, a general report will be prepared containing a recommended standard format, or audit protocol, for performing waste reduction audits at metal finishing plants. This protocol will serve as a guide for self audits by plant managers to undertake at their own plants.

WASTE STREAM INFORMATION ACCUMULATION AND ANALYSIS PROJECT

In order to better assess the potential for waste reduction, treatment, storage, disposal, and recycling facility needs, and compliance with the land disposal restrictions, DHS is setting up a program to collect and analyze data accumulated from the 1987 Biennial Generator and Annual Facility Reports. The information will provide DHS and industry with a better idea of compositions and volumes of hazardous wastes, remaining landfill capacities, existing treatment and storage capacities, and the potential for waste minimization activities in the State.

One project of this program would involve an update and revision to the Handbook of Industrial Waste Compositions in California. The Handbook, last prepared in 1978, will organize waste compositions and volumes according to Standard Industrial Classification (SIC) codes, RCRA waste codes, and California Waste Codes (CWC's) and present this in a final report.

A second project will determine the treatment, storage, and disposal capacity of on- and off-site facilities by county. Total tonnages of wastes handled and the total capacity in tons for each of the handling methods employed will be collected and analyzed. A final report summarizing these results will be produced.

A third project will provide information necessary for the development of treatment standards. Information related to quantities of hazardous wastes generated by RCRA and/or CWCs, and the individual or sequential handling methods employed in the management of those wastes will be collected and analyzed. This data will also be used in conjunction with the component information to establish a baseline for assessing the impact of future disposal restrictions on resource recovery, product substitution, and other waste minimization activities.

SOURCE REDUCTION PROJECT

A 2-year project entitled **"Quantification of Halogenated Solvent Waste Reduction Potential"** was started by the Source Reduction Resource Partnership (SRRP), a joint venture of the Metropolitan Water District of Southern California (MET) and the Environmental Defense Fund (EDF). The primary aim of the study is to estimate the potential for source reduction of chlorinated solvents of the principal solvent using industries in the 6 county area served by the MET.

Profiles on 14 high solvent using industries will be developed by gathering information from published literature sources and interviews with industry representatives. The profile will include detailed descriptions of chlorinated solvent use, waste generation, and waste management. Some of the industries to be investigated include vapor degreasing, electronics, adhesives, textile processing, paint stripping, and pesticides.

An initial list of source reduction options based on the industry profile will be generated for each of the industries. Based on the industry profiles and the source reduction options, a survey for field visits and telephone interviews will be developed and around 100 firms in the high solvent using industries will be visited and interviewed. The survey will then be updated and additional source reduction options will be documented and considered. An additional 100-200 solvent using firms will be surveyed with the results of all interviews and site visits being placed on a computerized data base. The source reduction options will then be analyzed and an estimate of costs associated with the implementation of these options will be made. These cost estimates will take into account the variation in the size of the industry.

Finally, institutional and other issues related to waste management and the regulatory environment which may affect the future implementation of source reduction practices will be analyzed. A partial list of issues to be examined include military specifications, small quantity generators, on-site recycling impediments, and assistance from large to small and medium firms in waste reduction.

SUMMARY

A better assessment of the waste reduction potential can be made after the collection and analysis of data related to the types and quantities of hazardous wastes produced and those methods available to handle the wastes. The information obtained from these EPA-funded projects will contribute to the DHS' more effective implementation of California's Waste Reduction Program.

REFERENCES

1. Winterlin, Wray, and Peterson, D. UV/hydrogen Peroxide Treatment for Destruction of Pesticide Laden Waste. Sept. 30, 1987. Dept. of Env. Tox., U. California, Davis. Report submitted to CA Dept. of Health Services, Toxic Subs. Cont. Div., Alt. Tech., Sacramento, CA.

THE EPA MANUAL FOR WASTE MINIMIZATION OPPORTUNITY ASSESSMENTS

by: Gregory A. Lorton, P.E., Jacobs Engineering Group, Pasadena, California
Carl H. Fromm, P.E., Jacobs Engineering Group, Pasadena, California
Harry M. Freeman, US EPA, Hazardous Waste Engineering Research Laboratory,
Cincinnati, Ohio

Waste minimization (WM) is fast gaining recognition as a means of contending with the nation's hazardous waste problem and other forms of environmental pollution. Opportunities exist for waste minimization throughout industry and government. The waste minimization assessment procedure described in this paper offers a means of determining a facility's waste situation, and identifying and evaluating potential viable options for reducing waste. This procedure has been developed by the authors for the US EPA and will be published in the EPA Manual for Waste Minimization Opportunity Assessments.

WHAT IS WASTE MINIMIZATION?

Waste minimization is comprised of source reduction and recycling. Source reduction is defined as any activity that reduces or eliminates the generation of waste at the source, usually within a process. Recycling is defined as the recovery and/or reuse of what would otherwise be a waste material. Figure 1 illustrates the various categories of waste minimization techniques.

The emphasis in this paper is on "hazardous waste". However, all waste streams must be considered when conducting an assessment. This includes air emissions, wastewater, and non-hazardous solid waste. The transfer of pollutants from one medium to another is not waste minimization.

INCENTIVES

There are a variety of incentives for minimizing wastes. These include the following

- Attractive economics (including reducing waste treatment and disposal costs, and savings in raw material costs)
- Increasing regulations (including landfill disposal regulations, reporting requirements, and permitting requirements for waste treatment)
- Reduced liability (including liability for environmental problems and workplace safety)
- Improved public image and environmental concern

The economic performance of WM projects has been enhanced in recent years by the dramatically increasing costs of waste disposal. Environmental regulations, especially RCRA (Resource Conservation and Recovery Act), have had a major effect on treatment and disposal costs.

THE WASTE MINIMIZATION ASSESSMENT PROCEDURE

The waste minimization assessment procedure presented here is a systematic framework that can be used by a facility's own employees to identify WM opportunities. As a structured program, it provides intermediate milestones and a step-by-step procedure to (1) understand the facility's wastes and processes, (2) identify options for reducing waste, and (3) determine which of the options are technically and economically feasible to justify implementation. On the other hand, the procedure should be modified to meet the specific needs of the individual company. As such, this manual should be viewed as a source of ideas and concepts, rather than a rigorous prescription of how to do assessments.

Figure 2 illustrates the WM assessment procedure. The WM assessment procedure is one part of a larger waste minimization program, which is required of hazardous waste generators. Careful planning and organization precedes the assessment itself. The assessment procedure can be split into two major phases:

- Assessment phase (collect information, and identify and screen potential WM options)
- Feasibility analysis step (technical and economic evaluation of the options)

Implementation of the recommended options follows the assessment. The WM program should be viewed as a continuing program, rather than a one-time effort.

PLANNING AND ORGANIZATION

Careful planning and organization is necessary to bring about a successful WM program. To start the program and maintain momentum and control, it is necessary to obtain management commitment. The program should set general goals by which to measure its effectiveness. Selecting a good program staff is critical to the ultimate success of the program. Since the program is a project organization within the company, a task force provides an effective way of carrying out the program. Table 1 describes important considerations involved in planning and organizing the program.

ASSESSMENT PHASE

The assessment serves to identify the best options for minimizing waste through a thorough understanding of the waste-generating processes, waste streams, and operating procedures. Therefore, the assessment task force's first major tasks are to collect information about the facility's waste streams, processes, and operations.

Collecting and compiling facility information

Information about the facility's waste streams can come from a variety of sources, such as hazardous waste manifests, biennial reports, environmental audits, emission inventories, waste assays, and permits. Mass balances should be developed for each of the important waste-generating operations to identify sources and gain a better understanding of the wastes' origins.

Collecting waste stream data and constructing mass balances will create a basis by which the assessment task can track the flow and characteristics of the waste streams over time. This will be useful in identifying trends in waste generation and will also be critical in the task of measuring the performance of implemented WM options later. The result of this activity is a catalog of waste streams that provides a description of each waste, including quantities, frequency of discharge, composition, cost of management, and other important information.

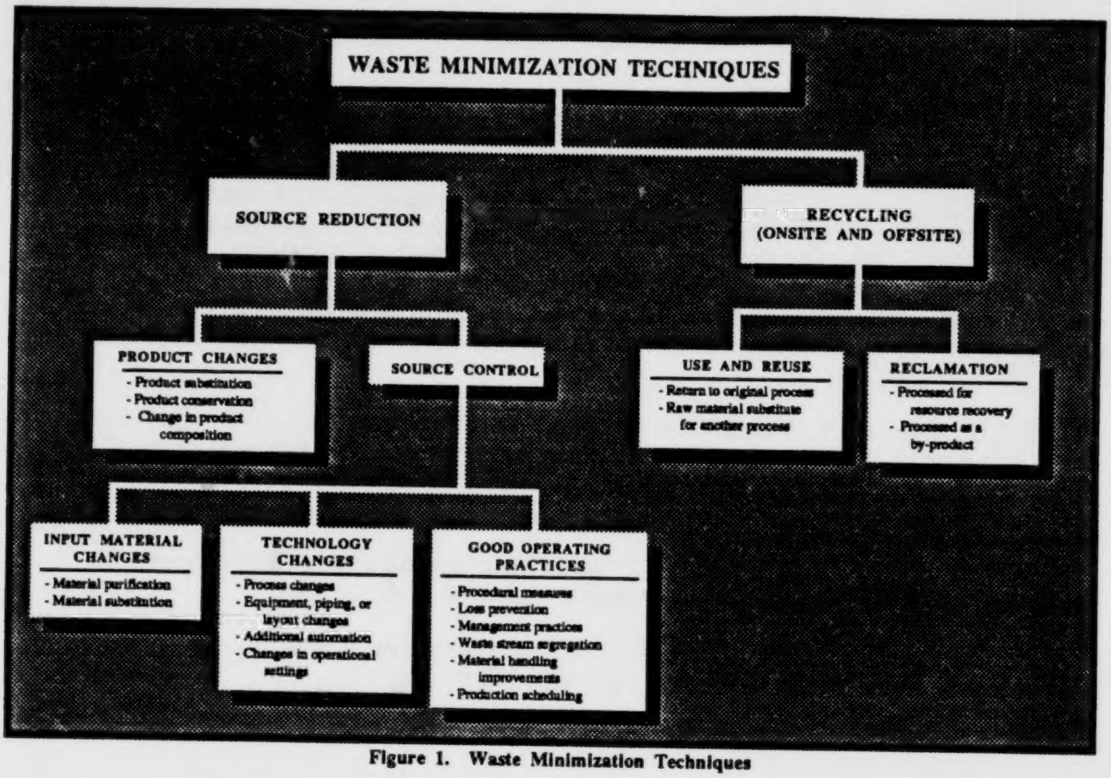

WASTE MINIMIZATION TECHNIQUES
SOURCE REDUCTION
RECYCLING (ONSITE AND OFFSITE)
PRODUCT CHANGES
- Product substitution
- Product conservation
- Change in product composition
SOURCE CONTROL
USE AND REUSE
- Return to original process
- Raw material substitute for another process
RECLAMATION
- Processed for resource recovery
- Processed as a by-product
INPUT MATERIAL CHANGES
- Material purification
- Material substitution
TECHNOLOGY CHANGES
- Process changes
- Equipment, piping, or layout changes
- Additional automation
- Changes in operational settings
GOOD OPERATING PRACTICES
- Procedural measures
- Loss prevention
- Management practices
- Waste stream segregation
- Material handling improvements
- Production scheduling

Figure 1. Waste Minimization Techniques

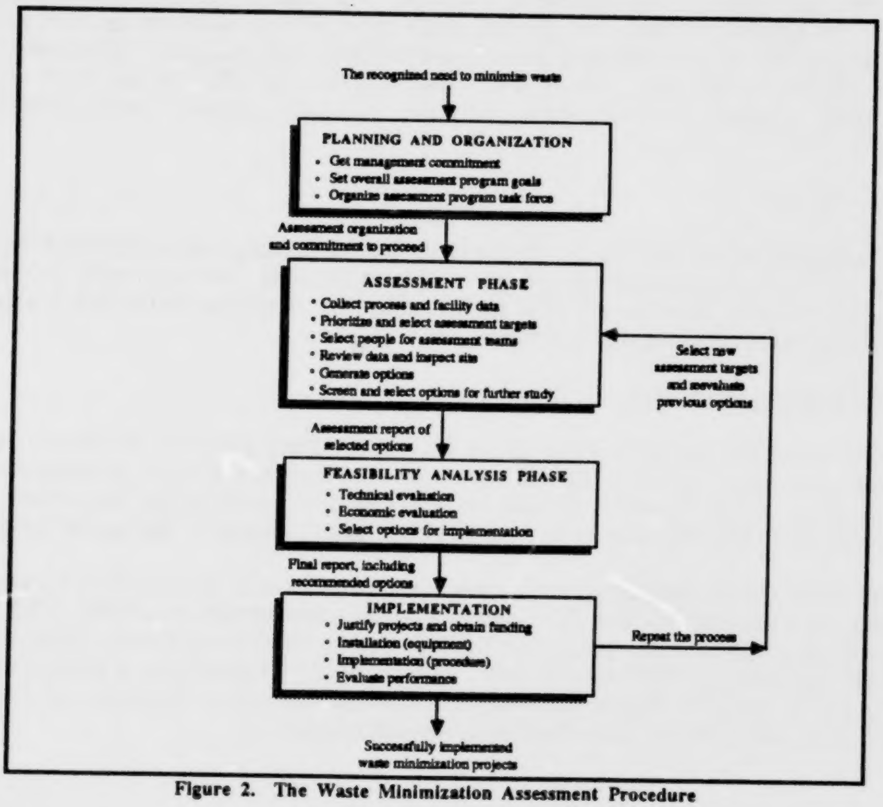

The recognized need to minimize waste
PLANNING AND ORGANIZATION
• Get management commitment
• Set overall assessment program goals
• Organize assessment program task force
Assessment organization and commitment to proceed
ASSESSMENT PHASE
• Collect process and facility data
• Prioritize and select assessment targets
• Select people for assessment teams
• Review data and inspect site
• Generate options
• Screen and select options for further study
Select new assessment targets and reevaluate previous options
Assessment report of selected options
FEASIBILITY ANALYSIS PHASE
• Technical evaluation
• Economic evaluation
• Select options for implementation
Final report, including recommended options
IMPLEMENTATION
• Justify projects and obtain funding
• Installation (equipment)
• Implementation (procedure)
• Evaluate performance
Repeat the process
Successfully implemented waste minimization projects

Figure 2. The Waste Minimization Assessment Procedure

TABLE 1. Planning and Organization Activities Summary

SETTING UP THE PROGRAM

Get management commitment to:
- Establish waste minimization as a company goal.
- Establish a waste minimization program to meet this goal.
- Give authority to the program task force to implement this program.

Set overall goals for the program. These goals should be:
- ACCEPTABLE to those who will work to achieve them.
- FLEXIBLE to adapt to changing requirements.
- MEASURABLE over time.
- MOTIVATIONAL.
- SUITABLE to the overall corporate goals.
- UNDERSTANDABLE.
- ACHIEVABLE with a practical level of effort.

STAFFING THE PROGRAM TASK FORCE

Find a "cause champion", with the following attributes:
- Familiar with the facility, its production processes, and its waste management operations.
- Familiar with the people.
- Familiar with quality control requirements.
- Good rapport with management.
- Familiar with new production and waste management technology.
- Familiar with WM principles and techniques, and environmental regulations.
- Aggressive managerial style.

Get people who know the facility, processes, and procedures.

Get people from the affected departments or groups.
- Production.
- Facilities/Maintenance.
- Process Engineering.
- Quality Control.
- Environmental.
- Research and Development.
- Safety/Health.
- Marketing/Client Relations.
- Purchasing.
- Material Control/Inventory.
- Legal.
- Finance/Accounting.
- Information Systems.

GETTING COMPANY-WIDE COMMITMENT

Incorporate the company's WM goals into departmental goals.

Solicit employee cooperation and participation.

Develop incentives and/or awards for managers and employees.

In addition to data about waste streams, other information is needed to fully understand the facility's operations. This includes the following items:

- Process, equipment, and facility design information
- Environmental reports, assays, manifests, documents, and permits
- Raw material and production information
- Operating cost information
- Policy and organizational information

Prioritizing and selecting waste streams to assess

Ideally, assessments should be conducted on all of the waste-generating operations in a plant. However, in larger plants this often is not practical, considering the limited resources (money, time, and expertise) available. In this case, the assessment program task force should prioritize the streams. Important criteria to consider in prioritizing waste streams and/or facility areas to assess include the following:

- Compliance with current and future environmental regulations
- Disposal cost and/or quantity of the waste
- Hazardous nature of the waste, and other safety considerations
- Potential for (and ease of) minimization
- Potential for removing production or waste treatment bottlenecks
- Available budget and expertise for the waste minimization assessment program

A practical consideration in selecting waste streams for the first assessment is to find those that can be reduced with a good likelihood of success. A successfully implemented WM project will insure the acceptance of further waste minimization efforts within the organization.

Select assessment team members

The assessment team must include people who are familiar with the area of the facility to be assessed. Including first line operators and production supervisors is recommended. These people may or may not already be on the assessment program task force. (In a large facility, the task force should have a broad understanding of the facility's operations, while the assessment team should have a specific understanding of the area to be assessed.) It may be advisable to include people from other parts of the facility that regularly interact with the area to be assessed.

Site Inspection

Although collecting and reviewing data is important in the assessment, the assessment team must be familiar with the actual operation at the site. To do this requires that the assessment team visit the site during the various stages or cycles of an operation. If all of the assessment team members work at the facility (or are located relatively close by) it is easy for the team members to visit the site. However, if one or more members are from outside of the facility, it is recommended that a formal site inspection be carried out.

The formal inspection serves to resolve all questions raised during the review and to complement that information already obtained and reviewed earlier. The inspection also confirms whether or not the facility actually operates in the way it was originally intended to. This inspection concentrates on understanding how the wastes are generated.

The assessment team should "walk the line" from the beginning of the process to the point where products and wastes leave the facility. Since waste can be generated in receiving and storage areas as well as the production areas, all areas within the site should be visited. The following guidelines will help in organizing an effective site inspection:

- Prepare an agenda in advance
- Schedule the inspection to coincide with the particular operation of interest.
- Monitor operations at different times during the shift.
- Interview operators, foremen, and supervisors. Assess the operating personnel's awareness of the waste generation aspects of the operation.
- Observe the housekeeping aspects of the operation. Assess the overall cleanliness of the site.
- Review the organizational structure and level of coordination of waste-related activities between the assessed facility area and other related areas.
- Assess the administrative controls.

Generating WM options

Following the collection of data during the assessment preparation step and the site inspection, the members of the assessment team will have begun to identify possible ways of reducing waste in the assessed area. The generation of options is both a creative and analytical process. While the individual assessment team members may be able to suggest many potential WM options on their own, the process can be enhanced by using some of the common group decision techniques, such as brainstorming. These techniques allow the team to identify options that the individual members might not have come up with on their own.

Identifying potential options requires the expertise of the assessment team members. Much of this knowledge comes from their education and on-the-job experience. Other sources of background information on potential options include the following:

- Trade associations
- Published literature
- Environmental conferences and exhibits
- Equipment vendors
- Plant personnel (especially the operators)
- Federal, state, and local government environmental agencies
- Consultants and/or employees from other facilities

Screening and selecting the most promising options for more detailed evaluation

A successful assessment will result in many WM options being proposed. At this point it is necessary to identify those options which offer a real potential to minimize waste and reduce costs. The screening procedure serves to eliminate those suggested options that are perceived as marginal, impractical, or inferior, without the detailed and more costly feasibility study. The procedures for screening these options can range from an informal decision made by the assessment program manager or a vote of the assessment team, to a weighted sum method that combines relative weights of such factors as operating cost reduction, capital cost requirement, reduction in waste hazard, etc.

Some options (such as procedural changes) may involve no capital costs and can be implemented quickly. The screening procedure should account for the ease of implementation for an option. If such an option is clearly desirable and indicates a potential cost savings, it should be considered for further study or outright implementation.

In screening the options, the assessment team determines what the important criteria are in terms of the WM assessment program goals and constraints, and the overall corporate goals and constraints. Examples of criteria that can be used include the following:

- Does the necessary technology exist to develop the option?
- How much will the option reduce waste quantity, hazard, and treatment/disposal costs?
- How much will the option reduce safety hazards?
- How much will the option reduce the use of input materials?
- What will the impact be on liability and insurance costs?
- How much does it cost? Is it cost effective?
- Can the option be implemented within a reasonable amount of time?
- Does the option have a good "track record"? If not, is there evidence that the option can work in this case?
- What other benefits will occur?

FEASIBILITY ANALYSIS PHASE

The WM options that are successfully screened in the assessment step then undergo a more detailed feasibility analysis. The feasibility analysis is not unlike that carried out for any new project within most organizations. However, there are some important characteristics to consider when evaluating waste minimization projects that are not necessarily considered with other types of projects.

Technical Evaluation

The purpose of the technical evaluation is to be sure that the option will really work as intended, and whether it can be implemented within specific facility constraints and product requirements. Typical criteria for the technical evaluation include the following:

- Will the option work in this application?
- How has it worked in similar applications?
- Is space available? Are utilities available? Or must new utility systems be installed?
- Is the new equipment or procedure compatible with the facility's operating procedures, work flow, and production rates?
- How long will production be stopped in order to install the system?
- Will product quality be maintained or improved?
- Is special expertise required to operate or maintain the new system? Does the vendor provide acceptable service?
- Does the system or procedure create or remove safety hazards?
- Does the system or procedure create other environmental problems?

All affected groups in the facility should contribute to and review the results of the technical evaluation. Prior consultation and review with the affected groups is needed to ensure the viability and acceptance of the option. If the option calls for a change in production methods, the effects on the quality of the final product must be determined. If the project appears infeasible or impratical after the technical evaluation, it is dropped.

Economic Evaluation

The economic evaluation is carried out using the standard measures of profitability, such as payback period or discounted cash flow techniques (internal rate of return and net present value).

Each company uses its own economic evaluation procedures and criteria for selecting projects for implementation. In performing the economic evaluation, various costs and savings must be considered. As in any project, the cost elements can be broken down into capital costs and operating costs.

Capital costs for WM projects are similar to most other projects. These costs include not only the fixed capital costs for designing, purchasing, and installing equipment, but also costs for working capital, permitting, training, start-up, and financing charges. As mentioned earlier, it is important to realize that some WM options, such as procedural or materials changes, will not have any capital costs. Also, many source reduction options have the advantage of not requiring environmental permitting in order to be implemented.

WM projects need to show a savings in operating costs to be economically effective. Operating costs and savings typically associated with WM projects include the following:

- Reduced waste treatment, disposal, and reporting costs
- Raw material cost savings
- Insurance and liability savings
- Increased costs (or savings) associated with product quality
- Decreased (or increased) utilities, operating and maintenance costs, and overhead costs
- Increased (or decreased) revenues from changes in production marketable by-products.

Once the capital and operating cost savings have been determined, the project's profitability can be determined using the profitability measures. These methods are discussed in virtually all financial management, cost accounting, and engineering economics textbooks. Those options that require no capital costs should be implemented as soon as savings in operating costs can be shown.

An important consideration for WM projects is their potential to reduce the risk of environmental and safety liabilities for a company. Although these risks can be identified, it is difficult to predict if and when liability problems will occur and the financial impact. It is important that the managers within the company who decide to fund the company's projects be aware of the significance of these risks and factor the risk reduction benefits of waste minimization into these projects. Also, while the profitability of a WM assessment program is important in deciding whether to implement a project, compliance with environmental regulations may be more important, since violation may ultimately result in shutting down the facility, and possible criminal penalties for the company's responsible people.

Final Report

The product of a WM assessment is a report that presents the results of the assessment and the technical and economic feasibility analyses. It also contains recommendations to implement the feasible options. A good final report can be an important tool for getting an attractive project implemented. The report should include not only how much the project will cost and its expected performance, but also how it will be done. Important topics to discuss include the following:

- whether the technology or procedure is established, with a mention of successful applications.
- the required resources (money, expertise, and manpower) available in-house, and those resources that must be brought in from outside.
- the estimated construction period and production downtime.
- the means by which performance can be evaluated after the project has been implemented.
- the reductions in environmental and safety liability.

Before the report is finalized, be sure to review the results with the affected groups. It is important to solicit the support of the affected groups. By having people from these groups assist in preparing and reviewing the report, the chances are increased that the attractive projects are successfully implemented.

IMPLEMENTATION

The implementation of the WM project is not unlike any other project that involves new equipment or procedures. It may be necessary to overcome inertia or resistance to change within the organization. The commitment of management to waste minimization is important at this time.

Once the project has been implemented and operating, it is important to evaluate its performance. Is it performing as expected? If not, should it be abandoned, or is its use still beneficial? What other potential options have been identified through the operation of this option?

ONGOING PROGRAM

The WM program should be viewed as a continuing one. As WM options are implemented, the task force should continue to look for new opportunities, assess other waste streams, and consider attractive options that were not pursued earlier. The ultimate goal is to reduce wastes to the maximum extent practical.

CONCLUSION

The waste minimization assessment offers opportunities to reduce operating costs, reduce potential liability, and improve the environment, while improving regulatory compliance. The WM assessment procedure results in a careful review of a plant's operations toward reducing wastes. The WM program task force should strive to build a waste minimization philosophy within the company. In doing so, the entire company can help to minimize waste.

CASE STUDIES OF WASTE MINIMIZATION ASSESSMENTS FOR CYANIDE WASTES FROM ELECTROPLATING OPERATIONS

by Deborah Hanlon and Michael Callahan
Jacobs Engineering Group
251 S. Lake Avenue
Pasadena, CA 91101
and
Thuy Le

ABSTRACT

Hazardous waste minimization opportunity assessments were conducted at two electroplating facilities generating cyanide-bearing wastes. The purposes of the two assessments were 1) to test assessment procedures and 2) to identify and prioritize waste minimization options for the cyanide-bearing wastes generated at the facilities. The procedures used for these assessments constitute those identified in the EPA Manual for Waste Minimization Opportunity Assessments, 1988.

This paper summarizes the waste minimization options developed and discusses the observations made as a result of the pilot assessments. Guidelines were formulated to assist in the execution of the waste minimization assessments and recommendations were made to improve upon their effectiveness.

At both facilities, over 23 options for minimizing cyanide-bearing wastes were considered. The options were screened and the highest ranking options were evaluated for technical and economic feasibility. The top-ranked options were reduction of drag-in and drag-out from the electroplating bath using drip boards, extension of bath life through filtration, reduction of water usage by spray rinsing, and waste stream segregation. A comparison of the options identified at both facilities is listed in Table 1.

The involvement of plant personnel in all phases of a waste minimization assessment was found to be essential to the acceptance of the recommended waste minimization options and to the implementation of ongoing waste minimization programs within the facilities. Effective communication and human interaction as well as technical insight and engineering skills were found to be essential for the success of the assessments.

TABLE 1

Summary of Options for Minimizing Cyanide Wastes at Facilities 1 and 2

Control Category	Control Methods for Facility 1	Control Methods for Facility 2
Drag-out Minimization	1. Proper positioning of parts on rack	1. Proper positioning of parts on rack
	2. Lower bath constituents concentration	2. Lower bath constituents concentration
	3. Reduce speed of withdrawal of parts	3. Reduce speed of withdrawal of parts
	4. Increase bath temperature	4. Increase bath temperature
	5. Use of surfactants	5. Use of surfactants
	6. Improve dragout recovery	6. Improve dragout recovery
Bath Life Extension	1. Dragin reduction by better rinsing	1. Dragin reduction by better rinsing
	2. Use deionized or distilled water	2. Use deionized or distilled water
	3. Bath impurity removal	3. Bath impurity removal
	4. Mechanical vs. air agitation	4.
	5. Proper rack design & maintenance	5. Proper rack design & maintenance
	6. Purer anodes	6. Purer anodes
	7. Proper anode removal	7.
	8. Return spent solution to manufacturer	8. Return spent solution to manufacturer
Rinse Water Minimization	1. Automatic flow control	1.
	2. Rinse bath agitation	2.
	3. Multiple rinse tanks	3. Multiple rinse tanks
	4. Fog nozzles and sprays	4.
	5. Close-loop rinsing & wastewater reuse	5.
	6. Proper barrel rinsing arrangement	6.
	7.	7.
	8.	8. Spray rinsing
Substitution of Non-cyanide Solutions	1. Pyrophosphate copper plating bath	1. Pyrophosphate copper plating solution
	2. Non-cyanide cadmium plating bath	2.
	3. Non-cyanide silver stripping solution	3. Non-cyanide silver stripping solution
Substitution of Plating Method	1. Cadmium ion vapor deposition	1.
	2. Aluminum ion vapor deposition	2.
Good Operating Practices	1. Waste stream segregation	1. Waste stream segregation
	2. Operator training/ closer supervision	2. Operator training/ closer supervision
	3. Spills and leaks prevention	3. Spills and leaks prevention
	4. Preventive/ corrective maintenance	4. Preventive/ corrective maintenance
	5. Management initiatives	5.
	6. Material/ waste tracking	6.
	7.	7. Removal of salts and dust
Alter Plant Layout	1.	1. Wastewater routing

BACKGROUND

The national policy objectives established under the 1984 Hazardous and Solid Waste Amendments to the Resource Conservation and Recovery Act include the goal of reduction or elimination of hazardous waste as expeditiously as possible. To promote these activities, the Hazardous Waste Engineering Research Laboratory (HWERL) of the U.S. EPA, Office of Research & Development undertook a project to promote waste minimization (WM) programs by developing and testing a WM assessment procedure. The postulated procedure was tested by conducting actual assessments in cooperating industrial and government facilities. The initially proposed procedure was modified to reflect insights and experience gained in the field, and was then used to develop the EPA Manual for Waste Minimization Opportunity Assessments, 1988.

The principal objective of a WM program is to reduce the quantity and/or toxicity of the waste effluents leaving a production process, in a manner consistent with the goals of protecting human health and environment. Unlike environmental audit programs, a WM program does not seek to determine or improve the regulatory compliance status of a facility. Rather, it is primarily oriented toward producing a set of effective measures to reduce waste generation.

The WM assessment is a central part of the WM program. The assessment steps include information gathering, selection of the assessment team, carrying out the assessment phase, and identifying and evaluating WM options. Since the assessment procedure is discussed in detail in the above-mentioned document, this paper will focus on the WM assessment results of the two plating facilities.

ASSESSMENT SUMMARY FOR FACILITY 1

DESCRIPTION OF FACILITY 1 PLATING PROCESS AND WASTE STREAMS

Facility 1, located in Southern California, is a major aviation, industrial, and seaport complex supporting anti-submarine aircraft, helicopters, and aircraft carriers of the Pacific Fleet. Cyanide wastes are generated from various operations associated with the facility plating shop. The principal metals plated at this facility are chromium, nickel, aluminum, copper, cadmium, and silver. Cyanide-based electroplating solutions involve copper, cadmium, and silver. Cyanide-based stripping solutions are used with silver only.

Plating is performed using racks or barrels. It is estimated that at least 75 to 85 percent of all surface area plated by the facility involves the use of racks. Barrels are used for plating small parts (such as screws) that do not lend themselves to rack mounting. While barrel-plating is used much less frequently than rack-plating, significant amounts of cyanide waste can be generated by this operation due to larger drag-out of plating solution.

Figure 1 represents a typical process flow diagram for the electroplating operation. For both rack-plating and barrel-plating, the sequence of steps is very similar. Because of the high degree of drag-out and the use of continuous filtering of the plating baths, routine batch replacement of the solutions is not required. Waste streams associated with the plating operation include spent alkaline solutions, alkaline rinse water, spent acidic cleaning solutions, acidic rinse water, plating tank filter waste, spent stripping solution, cyanide-containing rinse water, and inadvertent spills.

Cyanide losses occur primarily because of drag-out of plating/striping solutions (which then enter the wastewater), and from plating solution filtrate which is retained in the filtering medium and disposed of as hazardous waste. Wastewater from the cyanide sump is mixed with other waste streams and pumped to the Industrial Waste Treatment Facility (IWTF). It is estimated that approximately 650,000 gallons of wastewater are treated daily at the IWTF. About 5 percent of this is estimated to originate from cyanide-based plating operations. Approximately $350,000 is spent each year to dispose of 700 tons of wastewater treatment sludge. No attempt is made to recover precipitated metals from the sludge produced.

WASTE MINIMIZATION OPTIONS

After the site inspection, the assessment team identified numerous WM options for reducing cyanide wastes. The options developed for Facility 1 were grouped into six distinct categories. These categories included drag-out minimization, bath life extension, rinse water minimization, substitution of non-cyanide solutions, substitution of alternate plating metals or techniques, and good operating practices. The various waste minimization measures considered at the facility were ranked according to the method described in "Waste Reduction Audit Procedure" by Fromm and Callahan, 1986. The ratings were originally provided by project staff and then were reviewed by the staff of the host facility. Through a joint review of the ratings of each proposed waste minimization option, the top-ranking options were selected for additional evaluation and analysis.

A preliminary technical and economic feasibility evaluation was independently performed for 5 waste minimization options selected from among 23 options initially considered. Table 2 summarizes the results obtained from the economic analyses associated with the selected options.

Figure 1

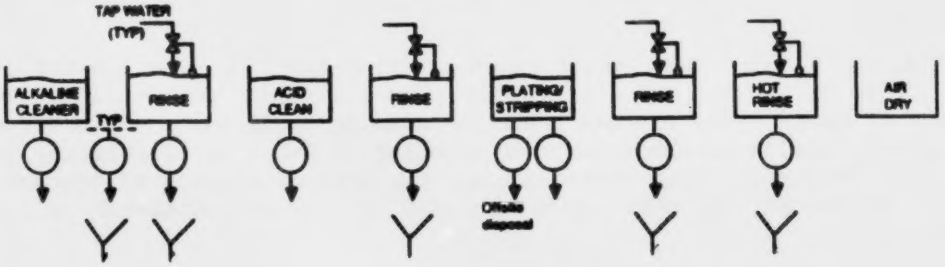


Table 2

Summary of Economic Feasibility Study for Facility 1

	Description of Options	Waste Reduction Method	Waste Reduction (%)	Capital Cost ($)	Monthly Cost ($/month)	Monthly Savings ($/month)	Pay-Back Period (month)	
1.	Drag-out Minimization	Use of Drain Boards	90	890	-	784	1.1	
		Use of Drain Boards/ impurity rempval	90	1103	1820	784	-	
		Use of Drain Boards/ Mechanical Agitation	90	7030	-	784	9.0	
		Still Rinsing						
		- Copper	40	560	-	202	2.8	yrs
		- Cadmium	40	1680	-	58	2.4	yrs
		- Silver	40	2800	-	89	2.6	yrs
2.	Bath Life Extension	Impurity Removal	-	213	1820	-	-	
		Mechanical Agitation	-	6140	-	-	-	
3.	Rinse Water Minimization	Spray Rinsing	50	11685	-	440	2.2	yrs

Drag-Out Minimization

The assessment team identified the option of reducing drag-out to minimize cyanide wastes generated at Facility 1. By minimizing the amount of drag-out carried from a plating, stripping, or cleaning bath to a rinsing bath, less of the plating solution constituents would leave the process, leading to savings in raw materials and treatment/disposal costs. The waste minimization techniques considered included the following:

- Bath concentration. Lowering the concentration of the plating bath will reduce the amount of cyanide and metal removed from the bath due to drag-out.
- Surface tension. The use of surfactants will lower the surface tension of the plating solutions and will reduce liquid clingage.
- Viscosity. Increasing the bath temperature will reduce the viscosity of the bath and reduce drag-out. This method will also aid in the ability to recycle water from a still rinse to the plating bath due to the higher rate of evaporation. Care must be taken, however, to ensure that the increase in temperature does not lead to break-down of the bath constituents.
- Physical shape and surface area of the workpiece. Rack mounted items should be positioned so that all recesses can drain properly.
- Workpiece withdrawal speed. Withdrawing the workpiece slowly from the plating solution will provide ample time for the part to drain.

- Drain boards. Drain boards can be installed to recover plating solution that would otherwise drag into the first rinse tank.

Further investigation of these options revealed that some of the drag-out minimization techniques (e.g. proper positioning of parts) were already well utilized in the facility. Others, (e.g. use of surfactants) did not rank high enough during the initial screening to deserve more attention. The installation and use of drainboards to minimize drag-out was the highest rated WM option in this category. This option would reduce wastes by 90%. The capital cost was estimated to be $895 and would result in a monthly saving of $784 from raw materials savings and avoided disposal costs. The resulting payback period would be 1.1 month.

Bath Life Extension

Extending the bath life of the plating solutions was identified as a potential WM option by the assessment team. The lifetime of a plating solution is controlled, among other factors, by the input rate of contaminants and/or by the rate of depletion of constituents due to drag-out. Depletion of constituents due to drag-out can be reduced by minimizing drag-out (discussed previously). However, many operators rely on excessive drag-out to remove bath impurities so some other means of impurity removal must be included when a facility employs drag-out reduction techniques. The following discusses the major sources of impurities and the ways to control or reduce them.

- Racks. Proper rack design and maintenance can help reduce the amount of corrosion that enters the bath.
- Anodes. Use of purer anodes, use of anode bags, and removing the anodes from the bath when not in use can reduce dissolution of the anode material into the bath.
- Drag-in. Proper rinsing of the parts before entering the bath can reduce drag-in of impurities and contaminants.
- Water make-up. Use of deionized water helps to prevent the build-up of certain minerals such as calcium or magnesium.
- Air. Use mechanical agitation instead of air agitation to avoid the build-up of carbon dioxide/carbonates.

After reducing the amount of impurities that enter the bath, additional control can be achieved by chilling the bath solution to freeze out carbonates, and therefore prolong the bath life. Another alternate solution for reducing plating bath waste is to return the solution to the manufacturer for reprocessing.

The WM options recommended for Facility 1 to extend bath life included conversion from air to mechanical agitation of the bath and to chill the bath solution to freeze out carbonates and other impurities. The capital costs for installation of mechanical agitation was estimated to be $7,030. The payback period is 9 months when calculated with drain board installation. The two options were combined since both must be implemented to assure product quality.

Rinse Water Minimization

The currently used procedure at the plating shop employs immersion of the workpiece in a single flow-rinse bath following a plating bath. Several methods exist which use less water than the flow-rinse method, while still adequately rinsing the workpiece. These are:

- Automatic flow controls.
- Rinse bath agitation.
- Multiple rinse tanks.
- Spray and fog nozzles.
- Closed-loop rinsing and rinse water reuse.
- Proper barrel rinsing arrangement.

Only the use of automatic flow control and the use of rinse bath agitation had been adopted at the facility. The installation and use of spray rinses to conserve water was recommended for Facility 1. With a capital cost of $11,685 the resulting payback period was estimated to be 2.2 years.

Non-Cyanide Substitutes

A variety of non-cyanide plating and stripping solutions can be used as substitutes for cyanide-containing baths. Such substitutes were tried on a limited basis without much success - the coating quality was judged as inferior to the one produced by cyanide solutions. Nevertheless, it was suggested that attempts be made to test the following new solutions, previously untried, on a small scale.

- Pyrophosphate copper plating solution.
- Non-cyanide silver stripping solutions.
- Non-cyanide cadmium plating baths.

Replacing cyanide solutions with non-cyanide solutions, however, would require the upgrading of the degreasing/cleaning step which precedes the plating or stripping operation. This is because the non-cyanide replacements have a much lower tolerance for impurities.

Procedural obstacles to the conversion from cyanide-based to non-cyanide-based solutions are the miliary specifications which spell out the requirement for the use of cyanide solutions. Modification of military specifications is regarded to be difficult and time consuming.

Good Operating Practices

Good operating practices (GOP) are defined as procedural or institutional activities that result in a reduction of waste generation. The

GOP recommended for this facility by the assessment team included the following:

- keep cyanide waste streams separate from other wastes;
- provide more operator training and closer supervision;
- equip all tanks with overflow alarms;
- routinely inspect for leaks, improve operational control for loading/unloading and transfer operations;
- isolate equipment or process lines that are not in service; and
- document the spillage and related dollar values for future improvements in clean-up procedures and prevention measures.

ASSESSMENT SUMMARY FOR FACILITY 2

DESCRIPTION OF FACILITY 2 PLATING PROCESS AND WASTE STREAMS

Facility 2 is a small privately owned electroplating shop located in Southern California. Their main business is refinishing decorative items. The principal metals plated at this facility are nickel, brass, silver, and gold.

Thirty tanks are used in cleaning and electroplating operations. The configuration of a typical plating unit includes a plating bath, followed by one or two still rinse tanks and a continuous rinse tank. Except for nickel plating, all plating/stripping solutions presently used at the facility are cyanide-based. All plating operations performed at the facility are performed manually.

Cyanide waste is generated from silver stripping; from silver, gold, brass, and copper electroplating; and from associated rinsing operations. The principal waste streams are wastewater (which includes overflows from the continuous rinse tanks and water used for floor washings), and plating tank filter waste. Aqueous streams generated from paint stripping, from metal stripping/electroplating, and from floor washings are routed to a common sump, then to the sanitary sewer.

In addition to sump sludge, solid waste is also generated due to the accumulation of metallic sludge inside the plating tanks, which is filtered out from the plating solution once a month using a portable dual cartridge filter. Two filter cartridges are used for each plating tank. Each filter cartridge is replaced approximately every 2 to 3 months. The contents of the sump (approximately 300-400 gallons of sludge containing dirt, stripped paint, cyanides, and heavy metals) are vacuumed out and disposed of as hazardous waste approximately once every 6 months. The total cost of waste collection, transportation, and disposal (per visit) increased from $2,000 to $4,000 after September 1986.

PROPOSED WASTE MINIMIZATION OPTIONS

After the site inspection was completed and additional information was reviewed, the team held a brainstorming session to identify potential waste minimization options for the facility. The following options were proposed during the meeting:

- Reduce solution drag-out from the plating tanks by:
  - Proper positioning of workpiece on the plating rack.
  - Increasing plating solution temperatures.
  - Lowering the concentration of plating solution constituents.
  - Increase the recovery of drag-out with drain boards.
- Extend plating solution bath life by:
  - Reducing drag-in by better rinsing.
  - Using deionized make-up water.
  - Using purer anodes.
  - Returning spent solutions to the suppliers.
- Reduce the use of rinse water by:
  - Using multiple countercurrent rinse tanks.
  - Using still rinsing.
  - Using spray or fog rinsing.
- Prevent dust from the adjacent buffing and polishing room from entering the plating room and contaminating the plating baths.
- Segregate cyanide wastes from the rinse tanks from other wastewater streams, such as floor washings and paint stripping wastes.

The team members each independently reviewed the options and then met to decide which options to study further. The team chose the following options for the feasibility analysis:

- Reduce drag-out by using drain boards.
- Extend bath life using deionized water for make-up.
- Use spray rinsing to reduce rinsewater usage.
- Segregate hazardous waste from nonhazardous waste.

FEASIBILITY ANALYSIS

The assessment team conducted technical and economic feasibility analyses on each of the four options. A summary of the economic feasibility for Facility 2 is shown in Table 3.

Table 3

Summary of Economic Feasibility Study for Facility 2

	Description of Options	Waste Reduction Method	Waste Reduction (%)	Capital Cost ($)	Monthly Cost ($/month)	Monthly Savings ($/month)	Pay-Back Period (month)
1.	Drag-out Minimization	Use of Drain Boards	50	315	--	241	1.3
2.	Bath Life Extension	Use of Deionized H_2O	50	582	38	241	2.9
3.	Rinse Water	Use of Spray Rinsing	50	2825	--	29	8.1 yrs
4.	Good Operating Practices	Use of Plastic Media Blasting	90	17900	2519/yr	6607/yr	4.4 yrs

Segregate Hazardous Wastes

The assessment team recognized that segregating hazardous wastes from nonhazardous wastes could be implemented at virtually no cost and would save money immediately. There were no identified technical problems.

Use Drain Boards to Reduce Drag-Out

Drain boards could be used to collect plating solution that drips off the rack and the workpiece after they are pulled out of the plating tank. The plating solution dryers from the part onto the board and drains back into the plating tank. This option reduces the concentration of cyanide in the rinse water and reduces make-up chemical consumption.

The purchase price of drain boards is estimated at $115, with installation costs of $200, for a total capital cost of $315. This option is expected to reduce rinse water disposal costs by $500 per year, and reduce make-up chemicals costs by $400 per year. The resulting payback period is 0.35 years, or about 4 months.

Use Deionized Water for Make-up Solutions and Rinse Water

Since the use of drian boards tends to dreduce the rate of impurity removal, use of DI water will help reduce the build-up or introduction of impurities into the plating bath. In particular, the build-up of minerals from tap water will be avoided. This, in turn, will avoid the precipitation of carbonates in the plating tanks.

The assessment team decided to combine the evaluation of this option with the previous option of using drain boards. The initial purchase and installation of a rented deionizer was $267. When adding the cost of the drain boards, the total capital cost of this option is $582. The deionizer is rented and serviced by an outside water treating service company for $450 per year. The savings in disposal costs and make-up chemical costs is $900 per year. Therefore, the annual net oprating cost savings is $450 per year. The payback period is 1.3 years.

Install Spray Rinses

Installing spray rinses would reduce the amount of rinse water required to clean the items. With spray rinse nozzles and controls, rinsing can be done on demand. Rinse water usage was estimated to be reduced by 50%. The resulting rinse wastewater is more concentrated and some can be returned into the plating tanks as a water make-up.

The assessment team determined that four spray rinse units would cost $2,120, plus an additional $705 for piping, valves, and installation labor. The total capital cost was $2825. The reduction in disposal costs were estimated at $350 per year, based on a 50% reduction in rinse wastewarer. This resulted in a payback of over 8 years.

Implementation

The procedures for segregating hazardous wastes from nonhazardous wastes was implemented before the feasibility analysis was completed for the other three options. The installation of drain boards and the purchase of a water deionizer were made shortly after the feasibility analysis was completed. The DI water system was online two months later. The results of implementing these options reduced the amount of waste from 800 gallons per year to 200 gallon per year.

CONCLUDING OBSERVATIONS

Some of the most important lessons learned in the pilot assessments relate to the human element of the assessment process, i.e., to the interaction between the assessment team and host facility personnel. It is imperative that host facility personnel become and remain active participants throughout the assessment process. This will help the company to establish the organizational structure, attitudes and information base necessary to sustain an ongoing waste minimization program. Some non-technical skills of the assessment team personnel, and particularly of the assessment team leader were found to be extremely important here. For example, the assessment team leader must be an effective and aggressive communicator, as well as a technical expert, because the team leader must play an important role as a facilitator for the assessment team and host facility personnel alike. In one case, a reserved and low key attitude and behavioral style of the assessment team initially led to a passive and relatively disengaged stance by the host facility personnel.

For both assessments, the availability of the required process documentation was not satisfactory. Flow diagrams were not available, neither were the design heat material balances, piping and instrumentation diagrams, and process descriptions. Other items were provided in stages, and in some cases, only partially. The availability and quality of information often varied significantly. It is important to make allowance for this possibility and to have a fall-back position. For example, if a piping and instrument diagram (P&ID) is not available, often times a piping layout plan will be. Similarly, if the information is not available from the facility, it does not mean that it cannot be obtained.

Much information is available from outside sources such as trade journals and vendors, e.g., the costs of bath make-up chemicals or the physical design of the process equipment. If information is truly needed but is not readily available, it can be obtained with proper initiative and ingenuity, but not without a possible detriment to project cost and schedule. In this light, it is important that only the information truly required to understand the process, to allow for delineation of waste sources and current waste management techniques, and to characterize waste generation quantitatively should be sought. Requesting unnecessary information burdens both the provider and user (auditor) and slows down the work.

The importance of the pre-assessment activities, particularly the pre-assessment site visits, were revealed as being extremely important in facilitating the assessment process. At a facility where the assessment team spent a little more time getting to know the host facility staff and how their organization functioned, the assessment process moved more smoothly. The assessment team found it easier and faster to acquire needed data because they knew better where (e.g., from whom) to obtain what data. Likewise, because they knew the operation and the people a little better, the level of cooperation by plant staff was improved.

It was observed during the assessments that while waste stream selection helped to sharpen the focus of the effort, such selection should always be open to review and reassessment. An excellent example is provided by the assessment of Facility 2. During the waste stream selection stage, the generation of the cyanide-bearing sludge in the sump was attributed to the electroplating operation. As waste minimization options were formulated, it was determined that the actual source of the sludge was from buffing and paint stripping operations (operations where cyanides are not used). Since total segregation of the cyanide-bearing electroplating waste and the non-cyanide-bearing sludges was impractical, the scope of the assessment was expanded to include options regarding sludge reduction and elimination.

The pilot studies experience led to a modification of the initially proposed assessment method. The initial approach of having the host facility personnel merely review and discuss the assessment team's ratings following the presentation of the option ratings resulted in a relatively casual attitude and less involved behavior by the host facility staff. To overcome this barrier, the modified approach required host facility personnel to independently develop ratings of each of the waste reduction options under consideration. The assessment team's ratings of the options and the host facility's independent ratings can then be reviewed and reconciled in a group session.

The pilot studies also revealed the importance of how assessment results (options and recommendations) are presented to plant personnel. In one case, when assessment team members were extremely comprehensive and detailed in describing and explaining the rationales for the options under consideration, plant personnel began to lose interest in the deluge of information. It also was found that Good Operating Practices (GOP) recommendations must be presented with tact. In one case, host personnel initially considered a number of GOP recommendations as trivial, and even a little insulting ("don't you think we know all that already"). However, this reaction changed considerably when the estimated cost savings for strictly adhering to these GOP measures were provided.

In summary, a WM assessment (and a WM program as a whole), requires effective communication and human interaction, as well as technical insight and engineering skills on the behalf of the assessment team members. A successful assessment is one that contributes to an on-going waste minimization program within the plant. Plant personnel will understand and focus on waste minimization rather than waste management. The generator will then be able to build upon the initial waste minimization assessment step to continue a program that can respond to changing technologies, costs and products.

ACKNOWLEDGMENT

The authors wish to acknowledge Carl Fromm (JEG), Harry Freeman (EPA), Fred Kirkpatrick (JEG), and the staff of the audited facilities for their assistance in the development of this project and paper.

BIBLIOGRAPHY

Durney, L.J., ed. 1984. Electroplating engineering handbook. 4th ed. New York: Nostrand Reinhold Co.

Fromm, C.H., and Callahan, M.S. 1986. "Waste Reduction Audit Procedure." A methodology for identification, assessment and screening of waste minimization options. Conference Proceedings. Atlanta, GA.: Hazardous Materials Control Research Institute.

Kahane, S.W. 1986. Waste minimization assessments. In Symposium on solvent waste reduction. Los Angeles, Calif.: ICF Consulting Assoc.

Lowenheim, F.A. 1979. Electroplating. In Kirk-Othmer encyclopedia of chemical technology. 3rd ed. Vol. 8. pp. 826-829.

McRae, G.F. 1985. In-process waste reduction: part 1. Plat. Surf. Finish. 72(6):14.

Olsen, A.E. 1973. Upgrading metal finishing facilities to reduce pollution. EPA-625-3-73-002. Washington, D.C.: U.S. Environmental Protection Agency.

Parkinson, G. 1979. Presenting - the energy audit. Chem. Eng. October 11. pp. 25-27.

Pojasek, R.B. 1986. Waste minimization - planning, auditing and implementation. In Monograph on Hazardous and Solid Waste Minimization. Washington, D.C.: Government Institutes Inc.

U.S. Congress 1986. Serious reduction of hazardous waste for pollution prevention and industrial efficiency. OTA-ITE-313. Washington, D.C.: U.S. Government Printing Office.

USEPA 1981. U.S. Environmental Protection Agency. Inplant changes for metal finishers. Cincinnati, Ohio: Industrial Environmental Research Lab.

____ 1981. U.S. Environmental Protection Agency, Office of Water Regulation and Standards. Development document for effient limitation, guidelines, and standards for the metal finishing point source category. EPA-440-1-83-091. Washington, D.C.: U.S. Environmental Protection Agency.

_____ 1986a. U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response. Report to Congress - minimization of hazardous waste. EPA-530-SW-86-042. Washington, D.C.: U.S. Government Printing Office.

_____ 1986b. U.S. Environmental Protection Agency. Waste minimization, issues and options. Vol. 1. EPA-530-SW-86-041. Washington, D.C.: Government Printing Office.

Williams, M.A. 1976. Organizing an energy conservation program. Chem. Eng. October 11. pp. 149-152.

TCLP AS A MEASURE OF TREATMENT EFFECTIVENESS: RESULTS OF TCLP WORK COMPLETED ON DIFFERENT TREATMENT TECHNOLOGIES FOR CERCLA SOILS

by: Robert C. Thurnau
U.S. Environmental Protection Agency
Cincinnati, Ohio 45268

M. Pat Esposito
PEI Associates, Inc.
Cincinnati, Ohio 45246

ABSTRACT

The 1984 Hazardous and Solid Waste Amendments (HSWA) of the Resource Conservation and Recovery Act (RCRA) require that EPA either ban the disposal of hazardous wastes to the land or ascertain that such wastes are acceptable for land disposal. The soil and debris associated with the clean up of Superfund sites also fall under these statutes and must be addressed. A significant part of the regulatory strategy adopted by EPA involved the determination of best demonstrated available technology for contaminated soils and debris. A series of soil treatment technologies that were considered as candidates for Superfund sites (physical, chemical, thermal solidifcation) were tested on a laboratory prepared feed sample and the waste product streams generated were processed by the Toxicity Characteristic Leaching Procedure (TCLP).

The TCLP chemicals and mechanism have been compared to some of the most severe leaching conditions experienced in the land disposal of hazardous wastes, and therefore the results of these tests should simulate the worst case situations. In this context, TCLP is being studied as an indicator of treatment effectiveness, and may be one of the criteria employed to determined if a waste is banned or land disposed. This paper presents the TCLP data generated from the five (5) different BDAT treatment technologies tested and helps to put the use of this technique into practical perspective.

INTRODUCTION

Under section 3001 of the Resource Conservation and Recovery Act (RCRA) EPA was charged with identifying those wastes which, if improperly managed, would pose a hazard to human health and the environment. The statute also specified that EPA identify such wastes through the development of lists of hazardous waste characteristics. Characteristics are those properties which, if exhibited by a waste, identify it as a hazardous waste, and are established for levels of which there is a high degree of certainty that the waste needs to be managed in a controlled manner. The Extraction Procedure Toxicity Characteristic (EPTox) was developed to determine if specified metals, inscctticides and herbicides could be mobilized from a simulated municipal sanitary landfill environment. As with most first generation rules, improvement and expansion followed. The Toxicity Characteristic Leaching Procedure (TCLP) was subsequently developed to address the mobility of a broad range of both organic and inorganic compounds and to solve the operational problems of the EPTC protocol.

The work reported in this paper centers around a set of soils that were synthetically prepared to simulate the soils found at a typical Superfund site. The soils referred to herein as Synthetic Analytical Reference Matrixes (SARM) were processed through five different treatment technologies: incineration, low temperature thermal desorption, chemical treatment, physical treatment and stabilization. The performance of each technology was evaluated by comparing total waste analysis (TWA) and TCLP analyses of the starting materials to the treated residues.

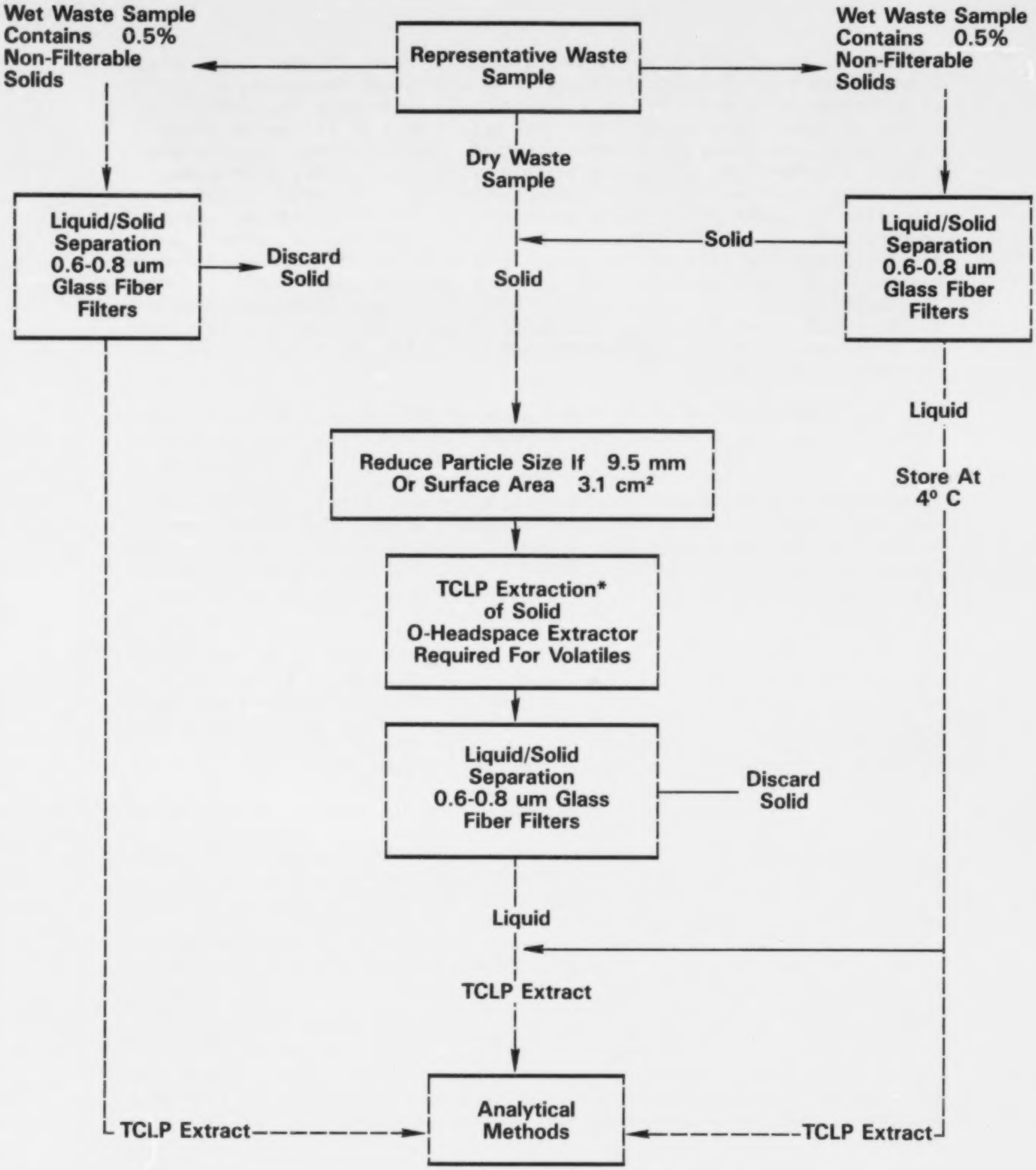
TOXICITY CHARACTERISTIC LEACHING PROCEDURE

A brief description of the TCLP is as follows: The sample is classified as liquid or solid by the percentage of solid material, reduced in size if necessary (<9.5 mm), weighed and mixed with an acidic solution at least 20 times the weight of the solid phase. The mixture is filtered and the extract is retained for chemical analysis. The procedure is modified somewhat when volatile organics are involved in that a zero headspace specific extraction vessel is required. A TCLP flow chart is presented as Figure 1.

EXPERIMENTAL

The basic composition of the soil used in the technology evaluations was determined as a result of an extensive literature search of Superfund records. The final soil composition selected consisted of (by volume): 30% by volume of clay (montmorillinite and kaolinite), 25% silt, 20% sand, 20% top soil and 5% gravel. The components were air dried, and then mixed

FIGURE 1. TCLP Flowchart


Representative Waste Sample
Wet Waste Sample Contains 0.5% Non-Filterable Solids
Wet Waste Sample Contains 0.5% Non-Filterable Solids
Dry Waste Sample
Liquid/Solid Separation 0.6-0.8 um Glass Fiber Filters
Discard Solid
Solid
Solid
Liquid/Solid Separation 0.6-0.8 um Glass Fiber Filters
Liquid
Store At 4° C
Reduce Particle Size If 9.5 mm Or Surface Area 3.1 cm²
TCLP Extraction* of Solid O-Headspace Extractor Required For Volatiles
Liquid/Solid Separation 0.6-0.8 um Glass Fiber Filters
Discard Solid
Liquid
TCLP Extract
TCLP Extract
Analytical Methods
TCLP Extract

---

* The extraction fluid employed is a function of the alkalinity of the solid phase of the waste.

together in two 15,000-lb batches in a standard truck mounted cement mixer. A prescribed list of chemicals found to be widely and frequently occurring at Superfund sites was added to the clean soil to produce the SARMs in a series of small scale mixing operations utilizing a 15 ft^3 mortar mixer. The organic components added were: acetone, chlorobenzene, 1,2-dichloroethane, ethylbenzene, styrene, tetrachloroethylene, xylene, anthracene, bis(2-ethylhexyl) phthalate and pentachlorophenol. The metals added to the clean soil were either salts or oxides of: arsenic, cadmium, chromium, copper, lead, nickel and zinc. Due to the fact that the contaminant profiles of Superfund soils differ widely from site to site in composition and concentration, four different SARM formulas were prepared. Table 1 presents the target contaminant concentration level of the four SARM samples as well as the actual level achieved. The SARMs showed representative consistency and homogeneity between formulations and approached the target levels outlined on Table I.

The SARMs produced in the first phase of this project were then processed through five treatment technologies that were thought to be most readily available and to have the greatest applicability to CERCLA site restoration activities. The technologies studied were: incineration, low temperature thermal desorption, chemical treatment (KPEG), physical treatment (soil washing) and solidification/stabilization. The effectiveness of the five different treatment technologies was measured by observing the change in concentration of the identified compounds and elements. TWA was used to measure changes in the total contamination levels in the treated SARM residuals as a result of treatment. TCLP on the other hand was used to track potential changes in leachate composition as a result of treatment. The logic behind the TCLP aspect of the project was that if the treatment reduces the total level of contamination or immobilizes it to a point where it will not migrate with the acidic leachate, the residual will be a good candidate for land disposal. Thus, residuals from each of the treatment technologies were collected and processed through the TCLP, and analyzed for the metals and organic compounds listed above.

RESULTS

Table II presents the results of the TCLP on the untreated soil SARM I. The data indicate that the semivolatile organic compounds were not efficiently extracted from the untreated soil. The volatile organic compounds were extracted at higher concentrations than the semivolatile organic compounds with the most volatile compounds (acetone and 1,2-dichloroethane) being extracted completely. Figure 2 shows a plot of the percent of volatile compound extracted by TCLP vs. the compound's boiling point. There appears to be a trend toward lower extraction of volatile organic compounds with increasing boiling point. The relatively lower water solubilities and high boiling points of the semivolatiles are a logical extension of this trend. This type of information would be useful in determining the minimum soil concentration levels that would be necessary for the use of TCLP as a predicting tool for organic compounds in residuals earmarked for land disposal.

TABLE 1

Target and Actual Concentrations For SARMs
Total Waste Analysis (TWA)

Table 1	SARM I mg/Kg		SARM II		SARM III		SARM IV	
Compound	Target	Actual	Target	Actual	Target	Actual	Target	Actual
(1) Acetone	6800	4353 ± 1933	680	357.0 ± 184.0	680	358.0	6800	3059
(2) Chlorobenzene	400	316 ± 49	40	13.2 ± 10.4	40	11.0	400	329
(3) 1,2-dichloroethane	600	354 ± 143	60	4.6 ± 3.8	60	4.9	600	491
(4) Ethylbenzene	3200	3329 ± 654	320	123.0 ± 111.0	320	144.0	3200	2708
(5) Styrene	1000	707 ± 96	100	48.0 ± 38.0	100	32.3	1000	631
(6) Tetrachloroethylene	600	459 ± 137	60	19.0 ± 11.0	60	20.1	600	540
(7) Xylene	8200	5555 ± 1921	820	165.0 ± 72.0	820	325.0	8200	5576
(8) Anthracene	6500	5361 ± 3785	650	353.0 ± 97.0	650	181.0	6500	1920 ± 1992
(9) Bis(2 ethylhexyl)phthalate	2500	1958 ± 1104	250	136.0 ± 120.0	250	114.0	2500	646 ± 284
(10) Pentachlorophenol	1000	326 ± 237	100	39.0 ± 55.0	100	30.0	1000	80 ± 23
(11) Arsenic	10	19 ± 7	10	17.4 ± 2.0	500	702.0 ± 204	500	562 ± 174
(12) Cadmium	20	23 ± 10	20	24.4 ± 3.1	1000	1934.0 ± 1352	1000	2897 ± 2819
(13) Chromium	30	26 ± 7	30	283.0 ± 5.0	1500	1204.0 ± 163	1500	1381 ± 172
(14) Copper	190	239 ± 56	190	259.0 ± 48.0	9500	9196.0 ± 1551	9500	11102 ± 1811
(15) Lead	280	245 ± 62	280	305.0 ± 58.0	14000	14695.0 ± 1507	14000	15178 ± 2227
(16) Nickel	30	33 ± 17	30	35.4 ± 15.2	1000	1419.0 ± 578	1000	1459 ± 616
(17) Zinc	450	502 ± 218	450	418.0 ± 179.0	22500	36177.0 ± 11878	22500	27428 ± 5472

TCLP SARM I Untreated Sample

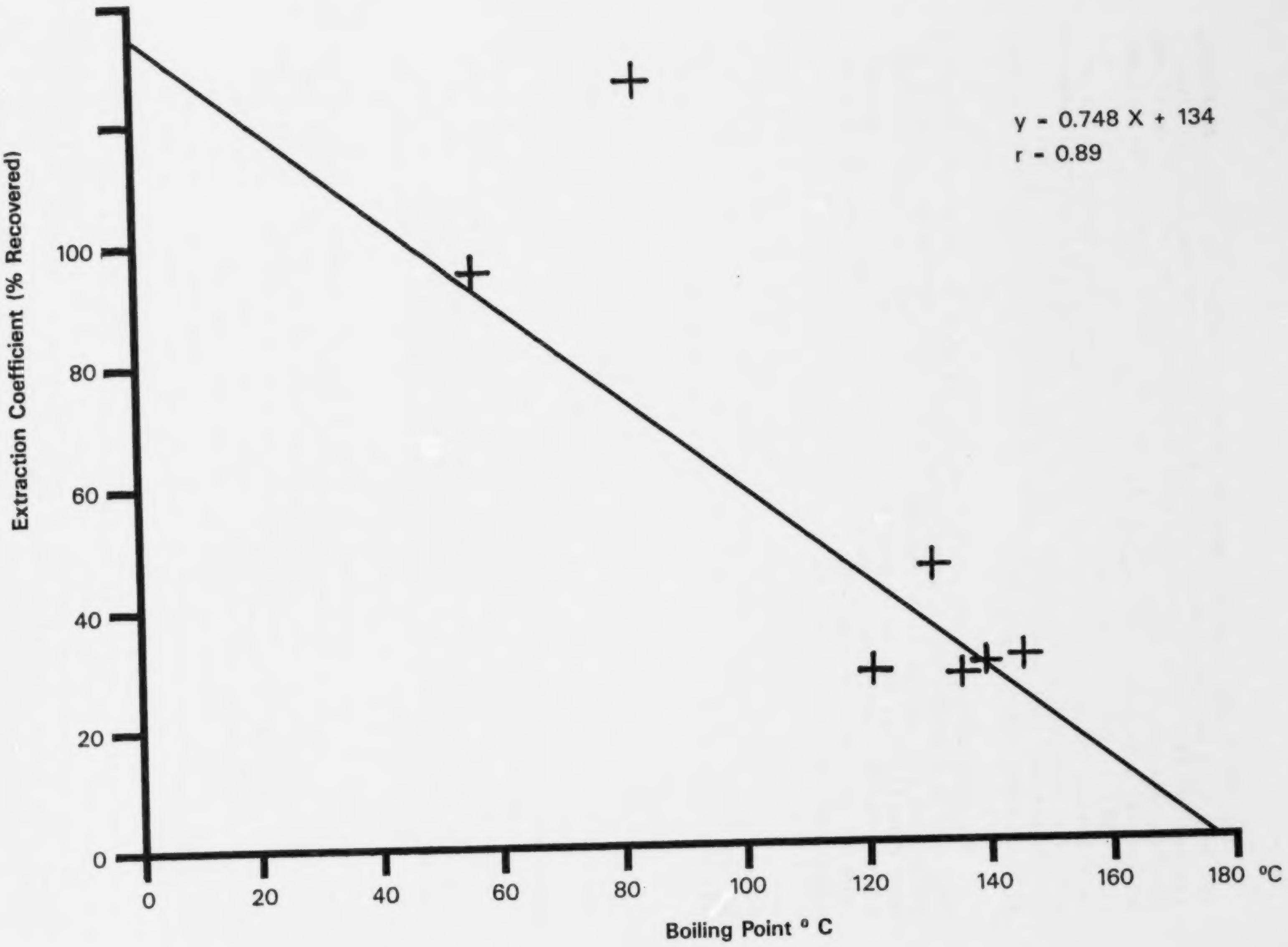
mg/L

Table 2

Compound	Soil Washing	PEI Associates QC Sample #1	PEI Associates QC Sample #2	Lee Wan Tech QC Sample #1	Lee Wan Tech QC Sample #2	Incineration Project	Mean of All Samples	Maximum Available For Extraction Taken	% TCLP Components Extracted
(1) Acetone	110.00	250.0, 260.0, 320.0	220.0, 230.0, 250.0	125.0, 155.0	134.00, 143.00	282.00	207.00 ± 70.00	218.00 ± 97.00	95.00
(2) Chlorobenzene	5.20	8.40, 7.90, 7.80	6.90, 7.50, 7.00	7.20, 7.20	7.70, 7.80	6.50	7.30 ± 0.80	15.80 ± 2.50	46.00
(3) 1,2-dichloroethane	76.00	27.00, 28.00, 27.00	26.00, 27.00, 27.00	17.00, 15.00	14.00, 18.90	19.00	22.30 ±5.50	17.70 ± 7.20	126.00
(4) Ethylbenzene	27.00	47.00, 45.00, 44.00	40.00, 44.00, 42.00	48.00, 61.00	44.00, 56.00	50.00	45.70 ± 8.40	166.50 ± 32.70	28.00
(5) Styrene	9.00	13.00, 13.00, 13.00	10.00, 11.00, 11.00	13.00, 12.00	12.00, 13.00	2.00	11.00 ± 3.10	35.40 ± 4.80	31.00
(6) Tetrachloroethylene	3.30	8.00, 7.20, 8.30	4.70, 5.80, 6.40	7.90, 7.50	7.70, 7.80	4.00	6.60 ± 1.70	23.00 ± 6.90	29.00
(7) Xylene	62.00	89.00, 84.00, 84.00	70.00, 76.00, 73.00	77.00, 98.00	78.00, 96.00	85.00	81.00 ± 10.50	277.80 ± 96.00	29.00
									54.90
*(8) Anthracene	70.00	5.00, 10.00, 15.00	20.00, 32.00, 31.00	10.00, 10.00	10.00, 10.00	10.00	19.42 ± 18.12	268.00 ± 189.00	< 0.01
*(9) Bis(2 ethylexyl)phthalate	100.00	5.00, 13.00, 11.00	26.00, 32.00, 31.00	20.00, 20.00	20.00, 20.00	60.0	26.50 ± 27.00	97.90 ± 55.20	0.02
(10) Pentachlorophenol	7.600	8.600, 5.000, 3.000	11.000, 4.100, 4.200	.250, .130	.180, 60.00	.980	4.09 ± 3.71	16.30 ± 11.90	23.00
									7.70
(11) Arsenic	0.15	0.02, 0.02, 0.02	0.02, 0.02, 0.02	0.15, 0.15	0.15, 0.15	0.15	0.09 ± 0.07	0.95 ± 0.35	9.00
(12) Cadmium	0.53	0.72, 0.72, 0.72	0.6, 0.73, 0.73	0.80, 0.79	0.82, 0.82	0.62	0.67 ± 0.21	1.15 ± 0.50	58.00
(13) Chromium	0.01	0.05, 0.04, 0.05	0.02, 0.06, 0.03	0.11, 0.13	0.12 0.11	0.01	0.06 ± 0.04	1.30 ± 0.35	5.00
(14) Copper	0.61	4.10, 3.30, 4.10	0.30, 3.90, 3.90	5.10, 5.20	5.20, 5.10	1.31	3.50 ± 1.80	12.00 ± 2.80	29.00
(15) Lead	0.49	1.90, 1.90, 1.80	0.08, 1.80, 1.90	2.70, 2.30	2.20, 2.10	0.46	1.60 ± 0.80	12.30 ± 3.10	13.00
(16) Nickel	0.27	0.64, 0.64, 0.64	0.04, 0.62, 0.65	0.70, 0.70	0.70, 0.71	0.34	0.55 ± 0.22	1.65 ± 0.85	34.00
(17) Zinc	9.20	13.60, 13.90, 13.80	1.00, 13.30, 13.50	16.40, 16.00	15.80, 15.80	7.96	12.50 ± 4.50	25.10 ± 10.90	49.00
									28.00

* ug/L

Figure 2 Boiling Point vs. Extraction Coefficient



The third area reported was the release of metals by TCLP. Although, the procedure was designed to simulate the worst case leachate, in these studies the TCLP only dissolved about 30 percent of the original metal into the leachate sample. Again, this is important from a sample selection and analytical detection limit standpoint. A sample like SARM I which has a relatively a high clay composition and a relatively low concentration of metals would not be a good choice for evaluating treatment effectiveness or metals as measured by metal mobility on the basis of TCLP. As the contamination level rises, the easier it becomes to evaluate both treatment effectiveness and TCLP mobility.

The main thrust of the project was to evaluate the treatment effectiveness of the five different technologies, by either destroying, removing or containing the pollutants of interest. One of the ways to judge the treatment effectiveness was to compare the leachability of the target compounds after treatment with similar data before treatment. TCLP was the vehicle selected to make this comparison. In making this selection it should be remembered that because the TCLP is not totally effective in extracting the different classes of compounds, the initial TCLP values for untreated SARMs were in several cases quite small and often near the limit of analytical detection. Thus in many cases the treatment effectiveness was judged on the difference between two small numbers. With these thoughts in mind, the TCLP data generated for the five CERCLA tratment technologies is presented.

Table 3 presents some typical TCLP data collected for the solidification experiments. SARM I was treated with portland cement, kiln dust and lime/fly ash and cured for 28 days. The stabilized materials were sampled, examined by TCLP and summarized. Each of the individual chemicals in the TCLP extract from the treated residuals were compared to the initial TCLP concentrations for the untreated SARMs and the individual removal efficiencies were calculated. Appropriate adjustments were made to account for dilution when the binders were added to the SARM. These efficiencies were summed and averaged for each class of compounds (volatiles etc.) and the average number taken as the treatment effectiveness attributable to TCLP. The bar graphs show the relationships for the different binders toward the same class of compounds.

The type of data illustrated in Table 3 can be expanded across all the technologies. Table 4 illustrates a typical TCLP data set for SARM I and how it was affected by each of the five treatment technologies tested. The TCLP data indicate that incineration did an excellent job of reducing the leachable organics in the residues. Surprisingly, the TCLP data for the metals in incineration ash are 83 to 99+ percent lower than the untreated SARM TCLP values, indicating that either metals were removed from the ash during the incineration process or that the ash was altered so as not to release as much metal in the TCLP test. Low Temperature Thermal Desorption at 150°F was only moderately effective on the volatiles, but at 350°F and was very effective. Semivolatile removal results exceeded 95% for anthracene and bis(2-ethyl hexyl) phthalate at all 3 temperatures; results for pentachlorophenol are somewhat erratic but seem to indicate the best removal rate (about 90%) at the 550° temperature. The metals data point toward a change in the soil matrix during heating which results in higher

Typical TCLP Data Summary For Solidification Experiments

Table 3

Compound	TCLP Regulatory Value mg/L	Initial Value As Determined By TCLP mg/L	SARM I Portland Cement	% Reduction	SARM I Kiln Dust	% Reduction	SARM I Lime/Fly Ash	% Reduction
(1) Acetone		207.00 ± 70.00	180.00	13.00	6.10	97.1	43.00	79.2
(2) Chlorobenzene	1.4	7.30 ± 0.80	1.30	82.20	0.06	99.2	1.60	78.1
(3) 1,2-dichloroethane	0.4	223.00 ± 5.50	< 0.44	> 98.00	0.10	99.6	< 0.10	> 99.6
(4) Ethylbenzene		45.70 ± 8.40	10.30	77.50	< 0.06	> 99.9	18.00	60.6
(5) Styrene		11.00 ± 3.10	< 2.80	> 74.50	1.06	90.4	4.10	62.7
(6) Tetrachloroethylene	0.1	6.60 ± 1.70	0.72	89.10	< 0.02	> 99.7	1.50	77.3
(7) Xylene		81.0 ± 10.50	13.80	83.00	2.04	97.5	22.00	72.8
				> 73.90		> 97.6		> 75.8
(8) Anthracene		19.80 ± 18.10	< 0.03	> 99.80	< 0.05	> 99.8	< 0.02	> 99.9
(9) Bis(2 ethylhexyl) phthalate		26.50 ± 27.00	1.02	96.20	< 0.05	> 99.8	0.16	99.4
(10) Pentachlorophenol	3.6	4.10 ± 3.70	3.87	5.60	< 0.13	> 96.8	0.40	90.2
				62.70		> 98.80		> 96.5
(11) Arsenic	5.0	0.09 ± 0.07	< 0.15	ND	< 0.15	ND	< 0.15	ND
(12) Cadmium	1.0	0.67 ± 0.28	< 0.01	> 98.50	< 0.01	> 98.5	< 0.01	> 98.5
(13) Chromium	5.0	0.06 ± 0.04	0.06	0.00	0.09	− 50.0	0.02	66.7
(14) Copper		3.50 ± 1.80	0.06	98.30	0.03	99.1	0.03	98.3
(15) Lead	5.0	1.60 ± 0.80	< 0.15	> 90.60	< 0.15	> 90.5	< 0.15	> 90.6
(16) Nickel		0.50 ± 0.22	< 0.04	> 92.70	< 0.04	> 92.7	< 0.04	92.7
(17) Zinc		12.50 ± 4.50	0.49	96.10	0.62	95.0	< 0.01	> 99.9
				95.20		95.2		91.1

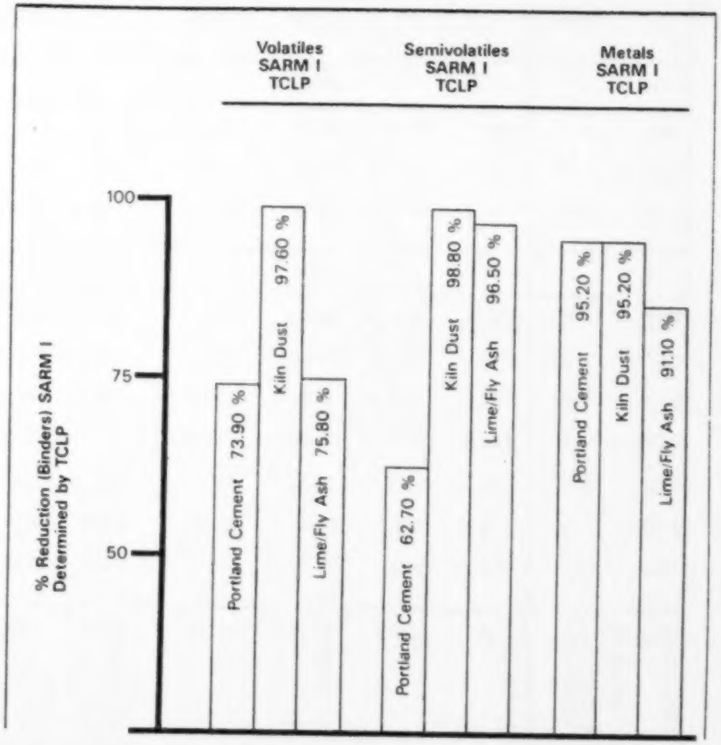


Table 4 Comparison of Treatment Technologies for SARM I Using TCLP

Compound	TCLP Data On Untreated Soil SARM I mg/L	-Incineration- Residue Generated By TCLP	% Reduction	Low Temperature Thermal Desorption						Chemical Treatment Residue	% Reduction
				150°	% Reduction	350°	% Reduction	550°	% Reduction		
(1) Acetone	207.00 ± 70.00	0.74	99.64	20.00	90.3	1.9	99.10	1.00	99.5	4.70	97.7
(2) Chlorobenzene	7.30 ± 0.80	< 0.04	> 99.50	2.90	60.3	<0.10	>98.60	< 0.10	> 98.6	0.76	89.6
(3) 1,2-dichloroethane	22.30 ± 5.50	0.10	> 99.60	0.40	98.2	<0.10	>99.60	< 0.10	> 99.6	<0.10	99.6
(4) Ethylbenzene	45.70 ± 8.40	0.65	98.60	44.00	3.7	<0.10	>99.80	< 0.10	> 99.8	8.10	82.3
(5) Styrene	11.00 ± 3.10	0.11	99.00	3.10	99.0	<0.10	>99.10	< 0.10	> 99.1	2.80	74.6
(6) Tetrachloroethylene	6.60 ± 1.70	0.04	> 99.40	1.30	80.3	<0.10	>98.50	< 0.10	> 98.5	<0.10	>98.5
(7) Xylene	81.00 ± 10.50	1.05	98.70	55.10	32.1	0.11	99.90	< 0.10	> 99.9	10.70	86.8
			99.21				99.23				89.9
(8) Anthracene	19.40 ± 18.10	< 0.01	> 99.90	< 0.02	>99.90	0.86	95.60	< 0.01	> 99.9	0.40	97.9
(9) Bis(2 ethylhexyl)phthalate	26.50 ± 27.00	< 0.01	>99.90	0.16	99.40	0.78	97.10	< 0.03	> 99.9	0.04	99.9
(10) Pentachlorophenol	4.09 ± 3.71	< 0.02	> 99.50	1.61	60.60	5.27	-28.80	0.35	91.4	1.10	73.1
			>99.80				54.60				90.3
(11) Arsenic	0.09 ± 0.07	< 0.15	ND	<0.15		<0.15	ND	< 0.15		<0.15	ND
(12) Cadmium	0.67 ± 0.28	< 0.01	>98.50	1.30		1.10	-64.20	0.90		0.40	40.3
(13) Chromium	0.06 ± 0.04	< 0.01	>83.00	0.10		0.13	-116.0	0.04		0.28	92.0
(14) Copper	3.50 ± 1.80	< 0.02	>99.40	6.80		5.13	-46.60	0.04		<0.01	>83.0
(15) Lead	1.60 ± 0.80	< 0.15	>90.60	2.80		2.30	-43.80	0.20		0.22	86.3
(16) Nickel	0.55 ± 0.22	< 0.04	92.70	1.40		1.10	-100.00	0.60		0.09	83.6
(17) Zinc	12.50 ± 4.50	< 0.03	>99.80	27.30		24.00	-92.00	13.80		3.25	74.0
			94.00				-77.10				76.5

Table 4 Comparison of Treatment Technologies for SARM I Using TCLP

		Soil Washing 2 mm to 250 um Surfactant		Solidification Kiln Dust	
Compound	TCLP Data On Untreated Soil SARM I mg/L	Residue Value mg/L	% Reduction	Residue Value mg/L	% Reduction
(1) Acetone	207.00 ± 70.00	0.65	99.7	6.10	97.1
(2) Chlorobenzene	7.30 ± 0.80	0.12	98.4	0.06	99.2
(3) 1,2-dichloroethane	22.30 ± 5.50	0.03	99.9	0.10	99.6
(4) Ethylbenzene	45.70 ± 8.40	0.97	97.9	<0.06	>99.9
(5) Styrene	11.00 ± 3.10	0.25	97.7	1.06	90.4
(6) Tetrachloroethylene	6.60 ± 1.70	0.10	97.4	<0.02	99.7
(7) Xylene	81.00 ± 10.50	2.20	97.3	2.04	97.5
			98.3		97.6
(8) Anthracene	19.40 ± 18.10	<0.02	>99.9	<0.05	>99.7
(9) Bis(2 ethylhexyl)phthalate	26.50 ± 27.00	0.10	99.6	<0.05	>99.8
(10) Pentachlorophenol	4.09 ± 3.71	0.41	90.0	0.13	96.8
			96.5		98.8
(11) Arsenic	0.09 ± 0.07	<0.15	ND	<0.15	ND
(12) Cadmium	0.67 ± 0.28	0.26	61.2	<0.01	>98.5
(13) Chromium	0.06 ± 0.04	<0.01	>83.3	0.09	-50.0
(14) Copper	3.50 ± 1.80	0.18	94.9	0.03	99.1
(15) Lead	1.60 ± 0.80	0.15	90.6	<0.15	>90.6
(16) Nickel	0.55 ± 0.22	<0.06	89.1	<0.04	>92.7
(17) Zinc	12.50 ± 4.50	1.90	84.8	0.62	95.0
			83.4		95.1

TCLP values after treatment compared to before, hence the negative removal efficiency values. This trend suggests that low temperature desorption may not be appropriate for soils containing both organic and metallic contamination. Chemical treatment by KPEG reduced the chlorinated volatile compounds (dichloroethane and tetrachloroethylene)by >98% and the semivolatiles by about >90%. KPEG treatment was also effective in reducing metals; TCLP values for metals in the residuals were overall 76.5% lower than for the the untreated SARM. For soils washing, treatment of 2 mm to 250 m fraction with surfactant reduced the volatiles in the TCLP by >98%, semivolatiles by >96%, and the metals by >83%. Stabilization utilizing kiln dust reduced the metals by >95%. The apparent high removal rates for organics (overall about 98%) following stabilization is thought to be the result of offgasing during mixing rather than the results of chemical reaction of the organics within the matrix.

The TCLP data collected around the five technologies, and four SARMs have been summarized in order of decreasing treatment effectiveness as shown in Table 5.

DISCUSSION

The TCLP system for evaluating the potential of a waste to release hazardous contaminants was based on manipulating laboratory extraction conditions until the results matched those from a pilot-scale system of lysimeters containing 90% municipal waste and 10% industrial waste. Its application to evaluating residues from different soil treatment options, or judging treatment efficiency of CERCLA soils should be approached with caution, and done on a case by case basis.

Each CERCLA site's soil will be different in some form and to this extent the degree to which the TCLP will extract each compound from the soil will also change. The attenuation of the individual compounds in the untreated SARMs by 70 to 95% places a terrific burden on the analytical techniques used to analyze the TCLP extract for two reasons. First, in many cases, even though the concentration of a given contaminant may be hundreds or thousands of parts per million in the untreated soil, the concentration produced in the leachate may lie at the fringes of the analytical detection limit; when compared to a leachate value derived from the treated residue, the two numbers may be virtually indistinguishable from each other. Thus the limits of analytical detection can prevent a true, picture from being formed regarding the effectiveness of a particular treatment. This type of condition can be clearly seen in the data for arsenic and chromium. Second and perhaps more importantly in many cases the treatment efficiency will be based on the difference between two small numbers. This was very evident in the metals data in Table 4 as well as all the metals data collected on all the synthetic soils. The solubility of inorganic compounds in an inorganic (i.e. aqueous) solvent system is the question that must be dealt with when using TCLP, and this data indicates that using this approach for evaluating treatment effectiveness could be risky.

However, when approaching TCLP from a health and safety standpoint with impacts on the environment being quantitated, the use of TCLP would

Table 5

TCLP Evaluation of Treatment Effectiveness for SARMs I, II, III, IV

	SARM I	% Reduction	SARM II	% Reduction	SARM III	% Reduction	SARM IV	% Reduction
Volatiles	(1) Low Temp Thermal Desorp @ 550° F	> 99.5	(1) Solidification Lime/Fly Ash 28 days	88.0	(1) Soils Washing +2 mm water	96.8	(1) Soils Washing +2 mm water	99.7
	(2) Soils Washing 250 um - water	99.5	(2) Incineration	> 82.8	(2) Soils Washing 250 um chelate	95.3	(2) Soils Washing +2 mm surfactant	99.3
	(3) Incineration	> 99.2	(3) Solidification - Kiln Dust - 28 days	82.0	(3) Soils Washing 2 mm to 250 um chelate	94.3	(3) Soils Washing 2 mm to 250 um water	99.1
	(4) Low Temp Thermal Desorb @ 350° F	> 99.2	(4) Low Temp Thermal Desorb @ 150° F	> 81.4	(4) Solidification - Kiln Dust - 28 day	> 93.6	(4) Soils Washing +2 mm chelate	99.1
	(5) Soils Washing 2 mm to 250 um - water	99.2	(5) Chemical Treat - KPEG (Test #1)	> 81.0	(5) Soils Washing 250 um - water	92.6	(5) Soils Washing 2 mm to 250 um surfactant	98.8
	(6) Soils Washing +2 mm - water	98.9	(6) Low Temp Thermal Desorb @ 350° F	> 80.8	(6) Soils Washing +2 mm - chelate	92.2	(6) Soils Washing 2 mm to 250 um chelate	98.6
	(7) Soils Washing +2 mm surfactant	98.8	(7) Low Temp Thermal Desorb @ 550° F	> 79.6	(7) Solidification Lime/Fly Ash 28 day	90.3	(7) Soils Washing 250 um surfactant	97.0
	(8) Soils Washing -2 mm to 250 um - surfactant	98.3	(8) Soils Washing - +2 mm chelate	73.4	(8) Chemical Treat KPEG - Test #1	84.2	(8) Chemical Treat KPEG - Test #1	96.2
	(9) Solidification - Kiln Dust - 28 day	97.6	(9) Soils Washing 2 mm to 250 um chelate	66.4	(9) Solidification - Port Cenebt - 28 day	68.3	(9) Soils Washing 250 um water	92.2
	(10) Soils Washing 250 um - surfactant	92.8	(10) Soils Washing 250 um - water	61.8			(10) Soils Washing 250 um chelate	80.7
	(11) Chemical Treatment KPEG (#1)	89.9					(11) Solidification - Kiln Dust 28 days	77.5
	(12) Solidification - Port Cement - 28 day	73.9					(12) Solidification Lime/Fly Ash	73.7
Semivolatiles	(1) Chemical Treatment - Test #1)	> 99.4	(1) Incineration	98.8	(1) Soils Washing +2 mm chelate	86.4	(1) Soils Washing +2 mm chelate	93.3
	(2) Solidification - Kiln Dust - 28 days	> 98.8	(2) Soils Washing +2 mm water	95.6	(2) Solidification Kiln Dust - 28 days	82.2	(2) Soils Washing +2 mm surfactant	92.6
	(3) Incineration	98.8	(3) Soils Washing +2 mm chelate	94.7	(3) Solidification Lime/Fly Ash - 28 days	54.8	(3) Solidification Lime/Fly Ash 28 day	88.6
	(4) Soils Washing +2 mm water	98.6	(4) Soils Washing +2 mm surfactant	94.7	(4) Soil Washing +2 mm - water	54.5	(4) Soils Washing +2 mm water	87.4
	(5) Soils Washing 2 mm to 250 um - surfactant	98.3	(5) Soils Washing 2 mm to 250 um water	92.9	(5) Chemical Treatment - KPEG Test #1)	50.5	(5) Chemical Treat KPEG Test #1	> 84.1
	(6) Soils Washing +2 mm - surfactant	98.1	(6) Low Temp Thermal Desorb @ 550° f	> 92.8	(6) Soils Washing 250 um chelate	31.8	(6) Soils Washing 2 mm to 250 um chelate	76.9
	(7) Low Temp Thermal Desorb @ 550° F	97.1	(7) Chem Treatment - KPEG - Test #1	> 91.0			(7) Soils Washing 2 mm to 250 um surfactant	70.0
	(8) Solidification - Lime/Fly Ash - 28 days	96.5	(8) Low Temp Thermal Desorb @ 150° F	> 89.5			(8) Soils Washing 2 mm to 250 um water	67.1
	(9) Low Temp Thermal Desorp @ 150° F	86.7	(9) Soils Washing 2 mm to 250 ug water	81.4			(9) Solidification Kiln Dust 28 days	52.7
	(10) Soils Washing 2 mm to 250 um - water	84.0	(10) Soils Washing 2 mm to 250 ug chelate	77.9				
Metals	(1) Solidification - Kiln Dust 28 days	> 95.1	(1) Soils Washing +2 mm - surfactant	96.4	(1) Solidification Port Cement 28 days	99.4	(1) Soils Washing +2 mm chelate	93.3
	(2) Incineration	> 94.0	(2) Soils Washing +2 mm chelate	94.7	(2) Soils Washing 2 mm to 250 um chelate	93.5	(2) Soils Washing +2 mm surfactant	92.6
	(3) Solidification - Lime/Fly Ash 28 days	> 92.3	(3) Soils Washing +2 mm water	94.6	(3) Soils Washing +2 mm chelate	88.7	(3) Soils Washing +2 mm water	87.4
	(4) Soils Washing +2 mm surfactant	88.6	(4) Soils Washing 2 mm to 250 um - chelate	92.2	(4) Soils Washing +2 mm water	87.4	(4) Solidification Port Cement 28 day	85.3
	(5) Soils Washing +2 mm water	87.4	(5) Solidification - Lime/Fly Ash 28 day	> 92.1	(5) Soils Washing 2 mm to 250 um water	84.1	(5) Soils Washing 2 mm to 250 um chelate	76.9
	(6) Soils Washing 2 mm to 250 um surfactant	83.4	(6) Solidification, Portland Cement 28 day	> 83.0	(6) Solidification Kiln Dust 28 days	83.7	(6) Soils Washing 2 mm to 250 um surfactant	70.0
	(7) Solidification, Port Cement 28 days	82.1	(7) Low Temp Thermal Desorp @ 150° F	82.0	(7) Solidification Lime/Fly Ash 28 days	54.3	(7) Solidification Lime/Fly Ash 28 day	68.3
	(8) Chemical Treat KPEG (#1)	> 70.1	(8) Soils Washing 2 mm to 250 um surfactant	74.2	(8) Chemical Treat KPEG - Test #1	35.0	(8) Soils Washing 2 mm to 250 um water	67.1
			(9) Solidification - Kiln Dust - 28 day	> 71.2			(9) Solidification Kiln Dust 28 day	66.4
			(10) Incineration	64.3			(10) Chemical Treat KPEG Test #1	48.7

be very useful. Table 3 shows the proposed TCLP Regulatory values for eight of the compounds listed (the other compounds have no current regulatory value proposed). The data in Table 3 indicate that the solidification binders of portland cement and lime/fly ash when used on SARM I could not bring the TCLP values for chlorobenzene, 1,2-dichloroethane, tetrachloroethylene and pentachlorophenol below the proposed regulatory limits implying that these compounds could still be released from the landfilled stabilized mixture in sufficiently high concentrations to have potential adverse impacts on the surrounding environment. The data in Table 4 also show that for SARM I low temperature thermal desorption at 150°F could release harmful concentrations of chlorobenzene, dichloroethane, tetrachloroethylene, and excessive cadmium could be released from the residuals regardless of the treatment temperature if land disposed after treatment. None of the residues from the other technologies had releases that would be flagged by TCLP standards.

Figure 3 expresses the TCLP data from Table 4 in bar charts by technology. This data can also be rearranged to study the treatment by compound class, and this is shown in Figure 4. When displayed in this manner, specific CERCLA problems can be isolated and the best treatment options selected.

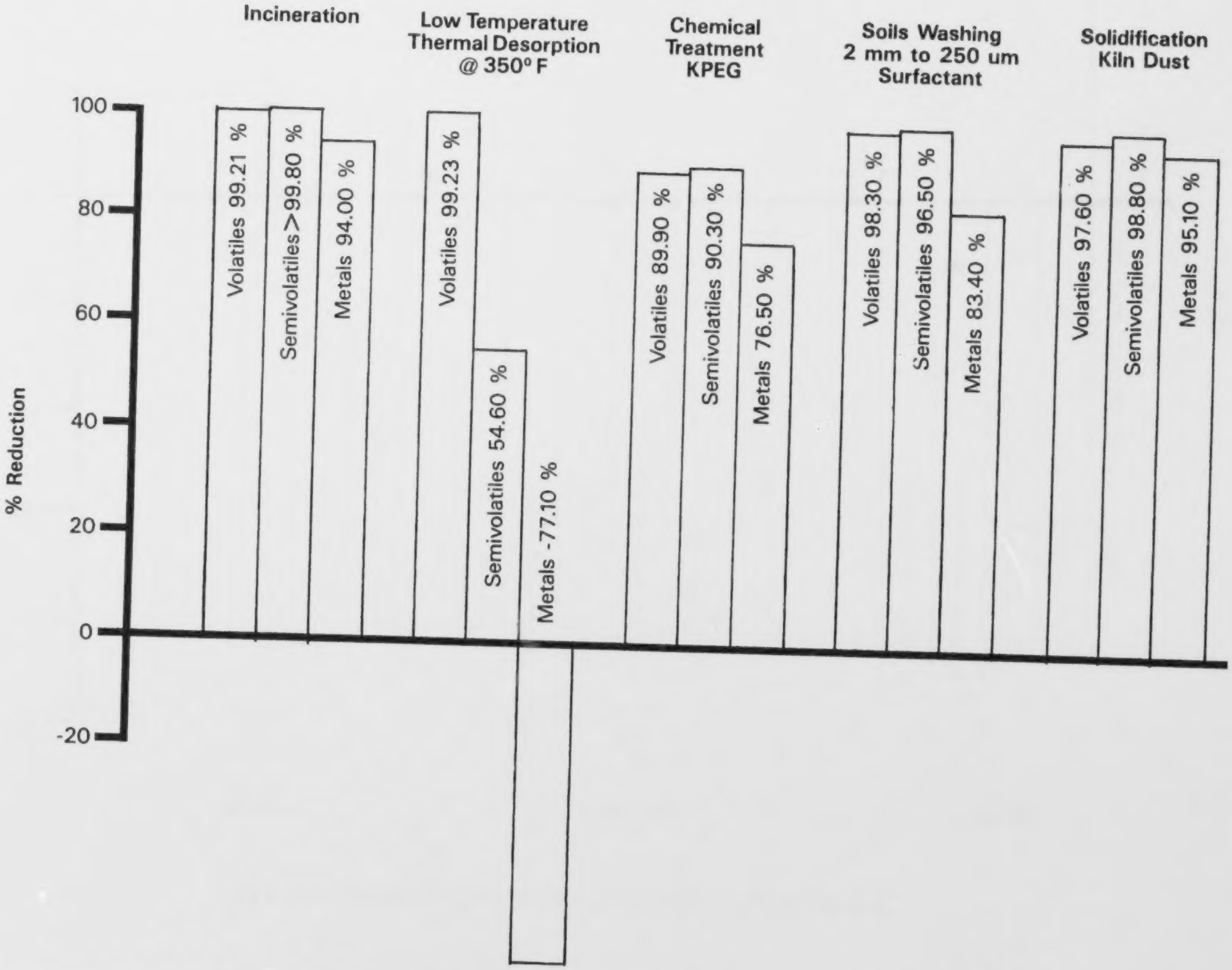
A logical extension of the TCLP work is to study how it compares with the data determined by total waste analysis (TWA) of the untreated SARMs and the tested residues. A series of parallel data sheets were developed for TWA that corresponded to the same sets of treatment options outlined for TCLP. Table 6 is a summary chart of the treatment efficiencies as measured by TWA for the different technologies in in decreasing order of effectiveness. Generally speaking, the thermal technologies did well against the organic fractions, chemical treatment and soils washing did well on the semivolatile fraction, and soils washing and solidification did well against the metals.

Figure 5 compares the effectiveness results of both TCLP and TWA for SARM I, for each technology by class of compound. For the volatile compounds, the TWA and TCLP data for treatment effectiveness were very close, and it didn't appear to make much of a difference which method was used for measuring treatment effectiveness. The TCLP/TWA percent effectiveness values for semivolatile organic compounds and metals appeared to be mixed, with generally higher effectiveness values associated with the TCLP data. Overall, TCLP as a measure of effectiveness gives at least equal and often higher results than TWA despite the fact that the initial concentration found in the TCLP leachate from the untreated SARM were more dilute than the TWA data by a range of 2 to 200 and some of the metals and semivolatile compounds were near the quantitation limit of the analytical equipment.

These findings, of course, are based on the treatment and analysis of residues from a freshly prepared synthetic soil. Comparable studies utilizing aged and weathered soils from actual Superfund sites are necessary to put these results into proper perspective. Such studies are currently in progress and results are expected to be available in late 1988.

TCLP Comparison of Treatment Options for SARM I

Figure 3



TCLP Treatment Comparison by Compound Class for SARM I

Figure 4

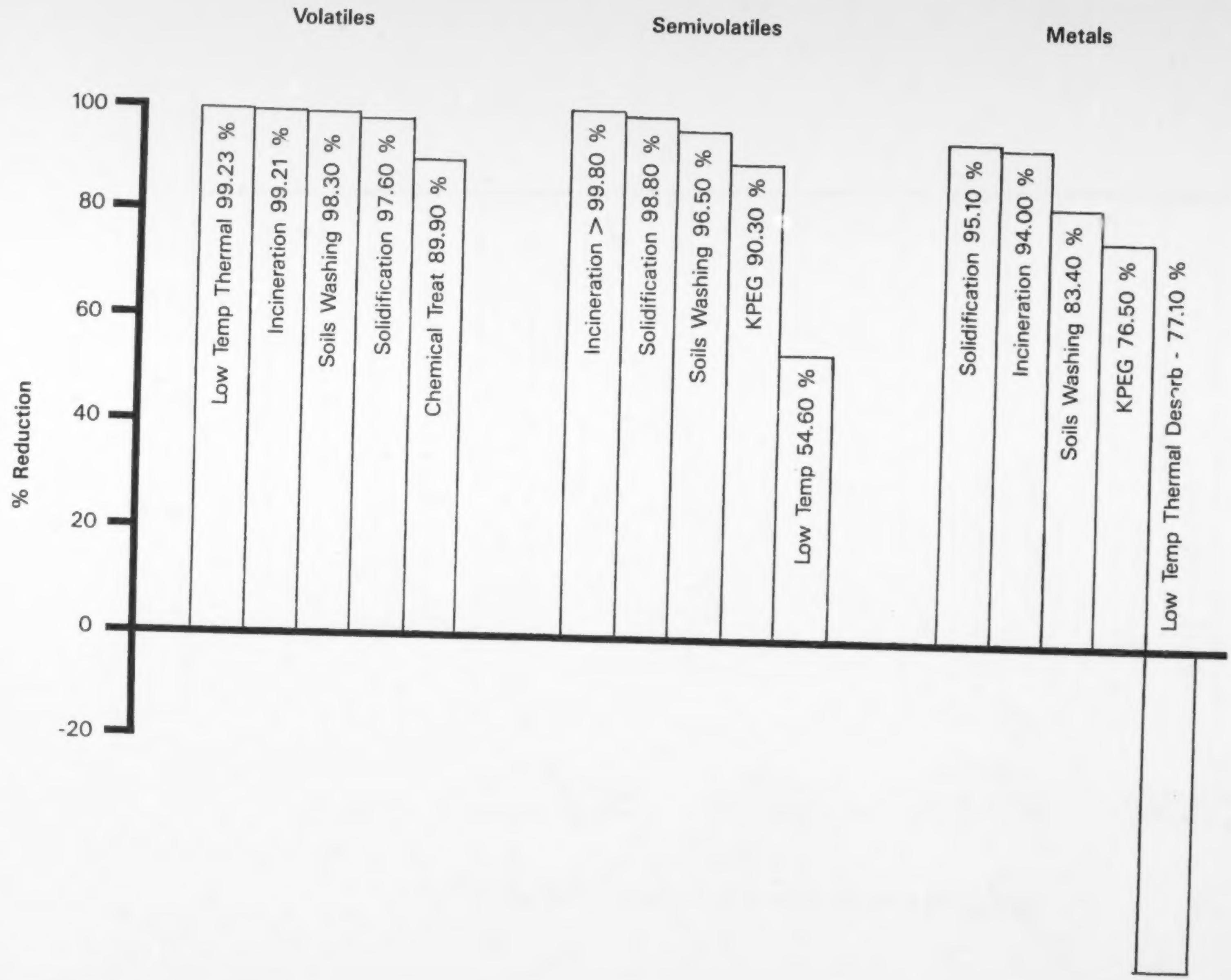


Figure 5. Comparison of Analytical Protocols for the Treatment of Soil (Metals)

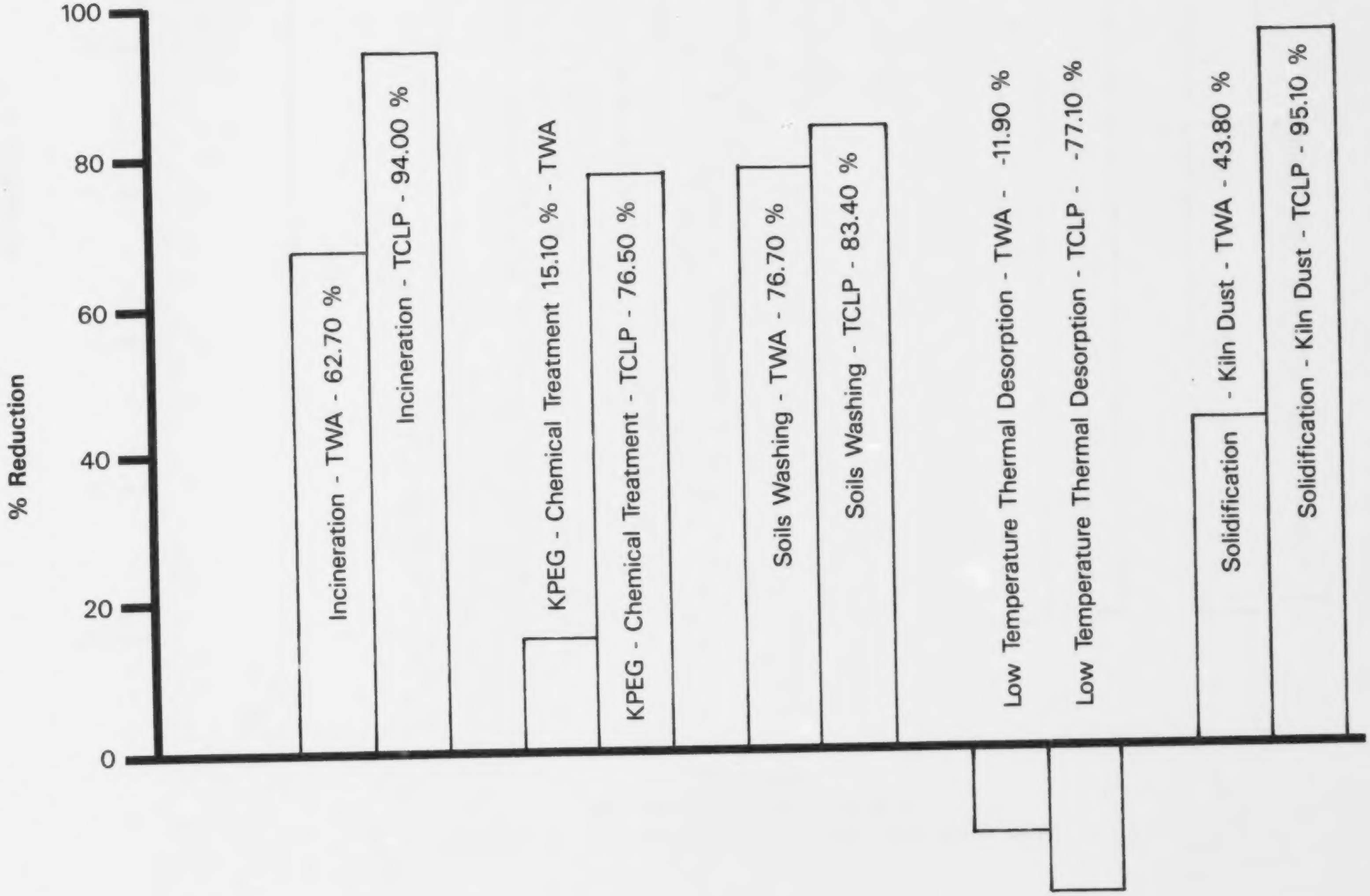


Figure 5. Comparison of Analytical Protocols for the Treatment of Soil (Volatiles)

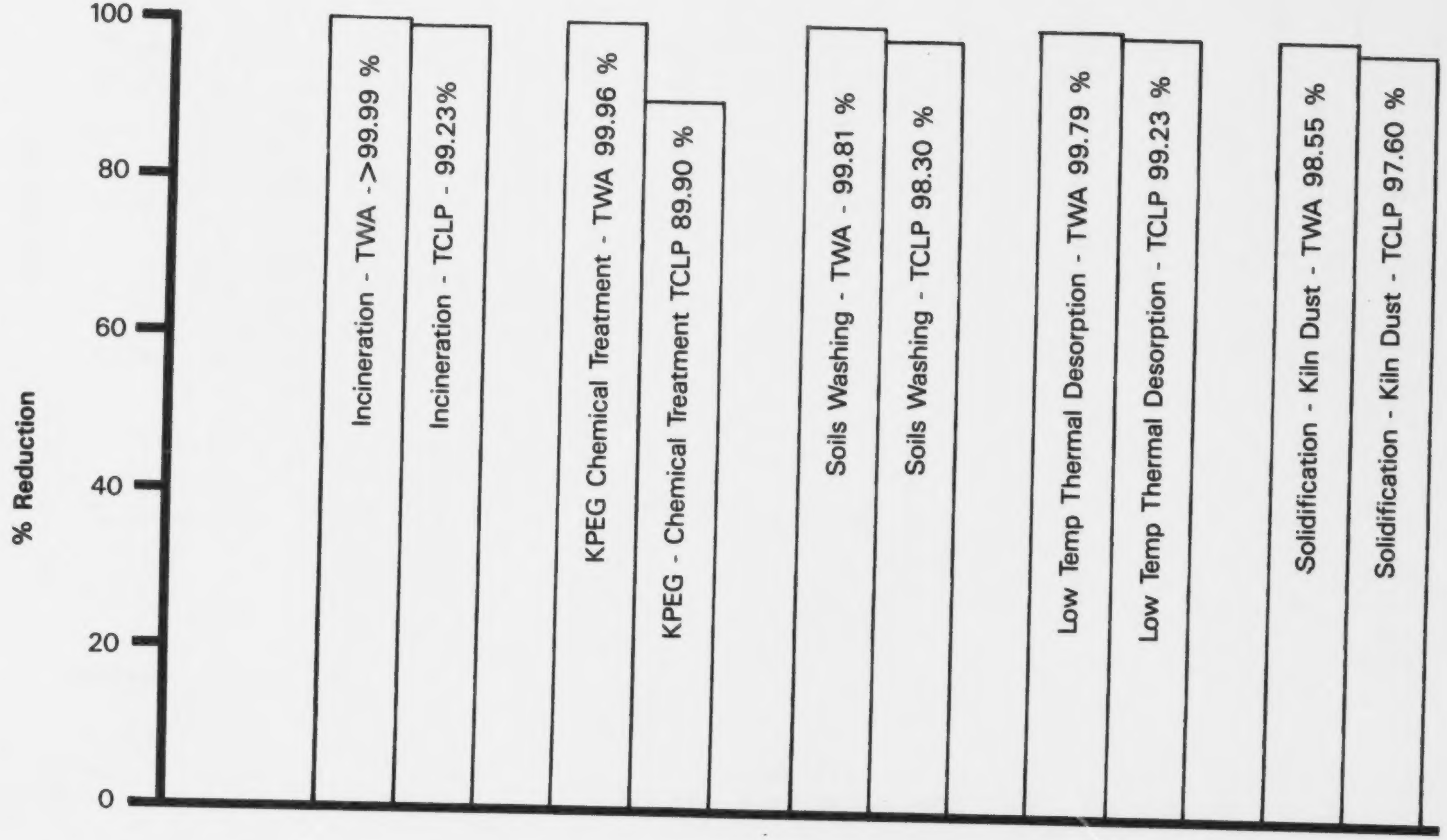


Figure 5. Comparison of Analytical Protocols for the Treatment of Soil (Semivolatiles)

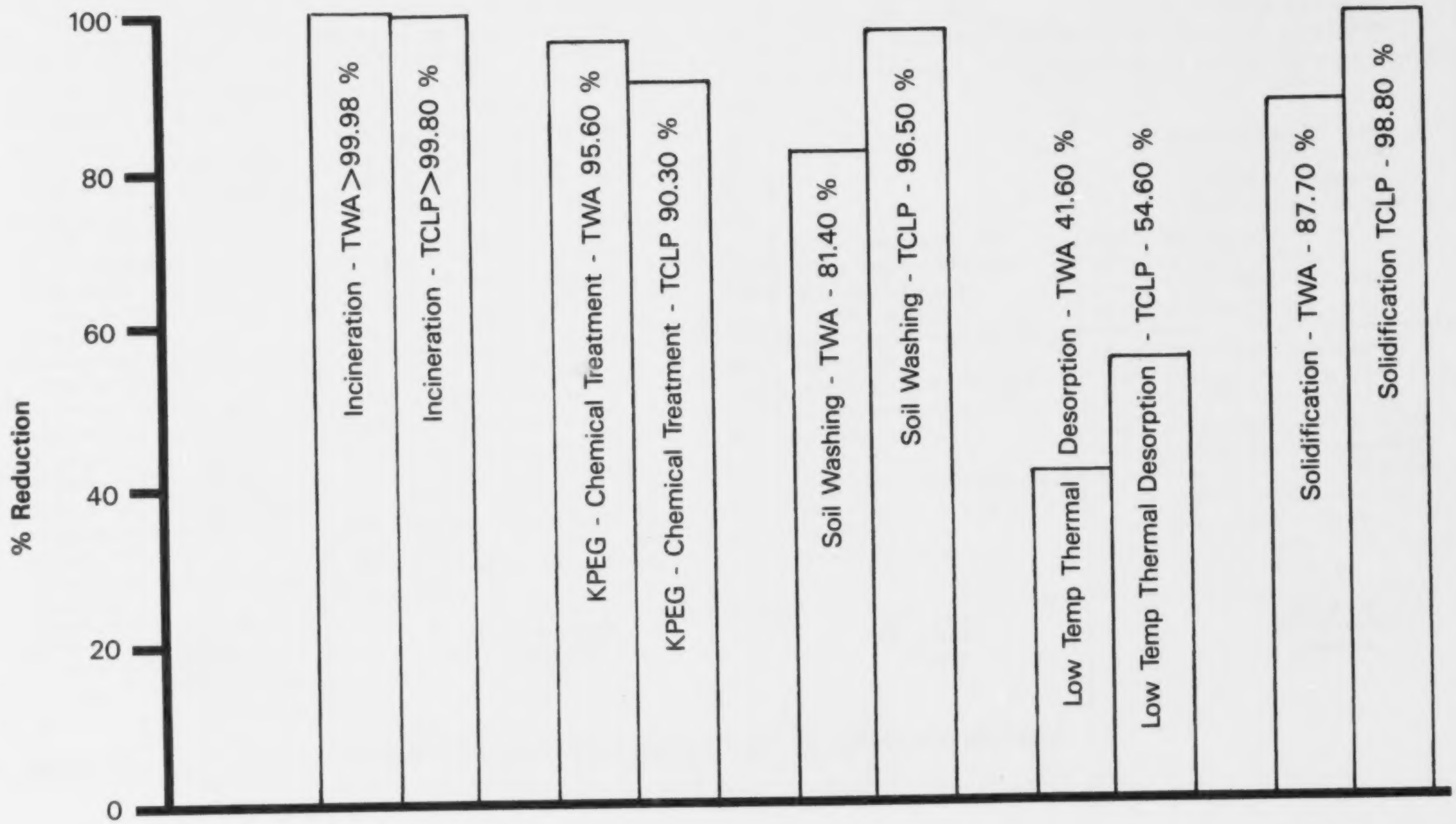


Table 6

Summary of Treatment Efficiencies as Measured by TWA

Table VI SARM I High Organics Low Metals		SARM II Low Organics Low Metals		SARM III Low Organics High Metals		SARM IV High Organics High Metals	
(1) Incineration	> 99.99	(1) Incineration	> 99.98	(1) Soils Washing +2 mm water	> 99.99	(1) Chemical Treat KPEG #1	99.98
(2) Soil Washing +2 mm water	> 99.90	(2) Soils Washing - all fractions - water	> 99.90	(2) Soil Washing +2 mm chelate	99.90	(2) Soils Washing +2 mm water	> 99.90
(3) Chem Treat KPEG #1	99.96	(3) Soils Washing - all fractions - chelate	> 99.70	(3) Chem Treat KPEG #1	99.50	(3) Soils Washing +2 mm chelate	> 99.90
(4) Soil Washing +2 mm surfactant	> 99.82	(4) Soils Washing - all fractions - surfactant	> 99.70	(4) Soil Washing 2 mm to 250 um water	99.30	(4) Soils Washing +2 mm surfactant	> 99.90
(5) Soil Washing 2 mm to 250 um surfactant	99.82	(5) Solidification - Kiln Dust 28 day	99.70	(5) Soil Washing 2 mm to 250 um chelate	99.00	(5) Soils Washing 2 to 250 um surfactant	> 99.70
(6) Soil Washing 2 mm to 250 um water	99.80	(6) Low Temp Thermal Desorb @ 150° F	98.70	(6) Solidification - Kiln Dust 28 day	98.10	(6) Soils Washing 2 to 250 um chelate	> 99.70
(7) Low Temp Thermal Desorb @ 350° F	99.79	(7) Chem Treat KPEG Test #1	98.20	(7) Chemical Treat KPEG #2	97.60	(7) Soil Washing 2 mm to 250 um water	> 99.70
(8) Low Temp Thermal Desorb @ 550° F	98.50	(8) Solidification - Lime/Fly Ash	97.00	(8) Soils Washing 250 um chelate	93.20	(8) Chemical Treat KPEG #2	98.10
(9) Solidification - Kiln Dust - 28 day	98.50	(9) Chem Treat - KPEG - #2	96.30	(9) Solidification Lime/Fly Ash 28 day	92.00	(9) Solidification Kiln Dust 28 day	95.30
(10) Chem Treat KPEG #2	98.30	(10) Low Temp Thermal @ 550° F	96.17	(10) Soils Washing 250 um water	86.70	(10) Soils Washing 250 um chelate	81.80
(1) Incineration	> 99.98	(1) Incineration	> 99.87	(1) Chemical Treat KPEG #1	99.60*	(1) Soil Washing +2 mm surfactant	> 98.30
(2) Soils Washing +2 mm surfactant	> 99.80	(2) Soils Washing +2 mm water	93.90	(2) Chemical Treat KPEG #2	99.00	(2) Soils Washing +2 mm chelate	97.80
(3) Soils Washing +2 mm water	> 98.90	(3) Soils Washing +2 mm surfactant	93.50	(3) Soils Washing +2 mm chelate	> 96.40	(3) Chemical Treat KPEG #2	96.20
(4) Chem Treat KPEG #2	97.00	(4) Soils Washing +2 mm chelate	90.10	(4) Soils Washing +2 mm water	> 94.8	(4) Chemical Treat KPEG #1	95.90
(5) Chem Treat #1	95.60	(5) Low Temp Thermal Desorb @ 550° F	88.93			(5) Solidification Lime/Fly Ash 28 day	47.90
(6) Low Temp Thermal Desorb @ 550° F	94.60	(6) Chemical Treat KPEG Test #1	83.80			(6) Soils Washing 2 to 250 chelate	32.30
(7) Soils Washing 2 mm to 250 surfactant	82.30	(7) Soils Washing 2 to 250 surfactant	67.50			(7) Soils Washing 2 to 250 surfactant	29.40
(8) Solidification Lime/Fly Ash surfactant	80.20	(8) Soils Washing 2 to 250 water	52.70			(8) Solidification Kiln Dust 28 day	28.30
(9) Solidification Kiln Dust	80.20	(9) Soils Washing 2 to 250 chelate	47.30				
(10) Soils Washing 50 um water	59.70	(10) Chem Treat KPEG #2	42.30				
(1) Soils Washing +2 mm water	92.20	(1) Soils Washing +2 mm water	> 96.70	(1) Soils Washing 2 mm to 250 um chelate	98.40	(1) Soils Washing +2 mm surfactant	98.40
(2) Soils Washing +2 mm surfactant	91.50	(2) Soils Washing +2 mm chelate	95.90	(2) Soils Washing +2 mm chelate	98.40	(2) Soils Washing +2 mm chelate	98.10
(3) Soils Washing 2 to 250 um water	81.60	(3) Soils Washing +2 mm surfactant	95.70	(3) Soils Washing +2 mm water	98.00	(3) Soils Washing +2 mm water	97.10
(4) Soils Washing 2 to 250 um surfactant	75.50	(4) Soils Washing 2 to 250 um chelate	91.60	(4) Soils Washing 2 mm to 250 um water	96.40	(4) Soils Washing 2 to 250 um surfactant	91.80
(5) Solidification Lime/Fly Ash 28 day	56.60	(5) Soils Washing 2 to 250 um surfactant	85.10	(5) Solidification Lime/Fly Ash	82.30	(5) Soils Washing 2 to 250 um water	90.70
(6) Solidification Kiln Dust 28 day	40.20	(6) Soils Washing 2 to 250 um water	82.70	(6) Soils Washing 250 um chelate	78.20	(6) Solidification Lime/Fly Ash	73.90
(7) Incineration	38.70	(7) Incineration	64.30	(7) Solidification Kiln Dust 28 day	73.20	(7) Solidification Kiln Dust	60.50
		(8) Chemical Treat KPEG #1	39.40	(8) Chem Treatment #1	49.40		

APPLICATION OF LOW-TEMPERATURE THERMAL TREATMENT TECHNOLOGY TO CERCLA SOILS

by:
Michael F. Szabo
PEI Associates, Inc.
11499 Chester Road
Cincinnati, Ohio 45246

Robert D. Fox
IT Corporation
312 Directors Drive
Knoxville, Tennessee 37923

Robert C. Thurnau
U.S. Environmental Protection Agency
Hazardous Waste Engineering
Research Laboratory
26 Martin Luther King Drive
Cincinnati, Ohio 45268

ABSTRACT

The U.S. Environmental Protection Agency (EPA) is evaluating best demonstrated available technology (BDAT) treatment levels for contaminated Superfund soils and debris for purposes of CERCLA/SARA compliance with the proposed 1988 Land Ban. The purpose of this project was to investigate the capability of a laboratory-scale low-temperature thermal desorption technology to remove volatile and semivolatile contaminants from a synthetically-prepared soil spiked with predetermined quantities of these contaminants.

A laboratory testing program was initiated, consisting of 15 separate bench scale tests (10 in a tray furnace and 5 in a tube furnace). The EPA synthetic soil of volatile and semi-volatile compounds (high and low, and a low concentration of metals in each soil) was tested at 150°, 350°, and 550°F for 30 minutes at temperature to determine the effect of this range of temperatures on removal of the contaminants. The tray furnace was used to determine the effectiveness of thermal desorption in removing contaminants from the soil. The tube furnace was used to provide data on the concentrations of contaminants in the off-gas for comparison with soil concentrations in an attempt to establish a material balance. This paper describes the thermal desorption test equipment and operating procedures, sampling and analysis procedures, analytical results, quality assurance and quality control, and conclusions drawn from the results of the study.

INTRODUCTION

INTRODUCTION

The U.S. Environmental Protection Agency's Office of Research and Development (ORD), in conjunction with Office of Solid Waste and Emergency Response (EPA-OSWER), is collecting data on treatment options for contaminated Superfund soils and debris. This work is being performed in the anticipation that the Hazardous and Solid Waste Amendments (HSWA) of 1984 will require that wastes generated from Comprehensive Environmental Response Compensation and Liability Activities (CERCLA) will require treatment to promulgated levels instead of being exhumed, transferred, and reinterred at a secured landfill. One of the technologies being investigated for the regulations is Low-Temperature Thermal Desorption. The purpose of the project reported in this paper was to investigate, on a laboratory scale, the capability of low-temperature thermal desorption technology to remove volatile and semivolatile contaminants from a prepared synthetic soil spiked with predetermined quantities of contaminants.

SOIL DESCRIPTION

The contaminated soil that was tested during this project was a surrogate Superfund soil containing a wide range of chemical contaminants typically occurring at Superfund sites. The surrogate soil is referred to as SARM, an acronym for synthetic analytical reference matrix. After considerable research into the types of soils found at Superfund sites nationwide, EPA decided on a soil composition of 30 percent by volume clay (a matrix of montmorillinite and kaolinite), 25 percent silt, 20 percent sand, 20 percent topsoil, and 5 percent gravel. These components were air-dried to minimize moisture and mixed together in batches in a standard truck-mounted cement mixer.

A prescribed group of chemicals found to be widely and frequently occurring at Superfund sites were then added to the clean SARM in a series of smaller-scale mixing operations. Organic chemicals added included ethyl benzene, xylene, 1,2-dichloroethane, perchloroethylene, acetone, chlorobenzene, styrene, anthracene, pentachlorophenol, and bis(2-ethylhexyl)phthalate. Salts or oxides of the following metals were also noted: lead, zinc, cadmium, arsenic, copper, chromium, and nickel. Due to the wide range of contamination in CERCLA soils, four different SARM formulas containing either high or low levels of organics and metals were prepared for use in various tests. The target concentrations of volatiles, semivolatiles, and metals that were added to the soils for use in this project are shown in Table 1.

TABLE 1. SARM SOIL TARGET CONTAMINANT CONCENTRATIONS

	SARM-I high, ppm	SARM-II low, ppm
Volatiles		
Ethylbenzene	3200	320
Xylene	8200	820
Tetrachloroethylene	600	60
Chlorobenzene	400	40
Styrene	1000	100
1,2-Dichloroethane	600	60
Acetone	6800	680
Semivolatiles		
Anthracene	6500	650
Bis(2-ethylhexyl)phthalate	2500	250
Pentachlorophenol	1000	100
Metals		
Lead	280	280
Zinc	450	450
Cadmium	20	20
Arsenic	10	10
Copper	190	190
Nickel	20	20
Chromium	30	30

Experimental

The principal test equipment was a Linberg Furnace, Model 51848, with an electronic temperature controller and 1600-watt heater system. The oven is of double-shell construction with interior surfaces made of Moldatherm, a molded aluminum-silicate insulation material. This oven, which is capable of operating up to 1100°C, has a relatively fast heatup rate because of its low mass.

The untreated sample materials (SARM) were analyzed by EPA Methods 8240, 8250/70, and 6010/7000 for the indicator compounds listed in Table 1. The characterized soil was sampled, weighed, and evenly distributed on an Incolay tray. The tray was inserted into the oven and connected to a nitrogen purge of 90 cm^3/min. Two thermocouples were used to measure temperature at 3 cm above the soil surface at the center of the tray.

The soils were treated at temperatures of 150°F, 350°F, and 550°F for thirty minutes, removed from the oven, cooled for one hour, and sampled. The samples were again analyzed by the same methods for the same compounds identified in Table 1, and the difference was attributed to treatment by low-temperature desorption.

The conditions under which the experiments were conducted are summarized in Table 2.

Results--

Tables 3 and 4 summarize the data generated on the treated and untreated SARM samples (I and II) processed by low temperature thermal desorption. The data indicate that low temperature treatment could be very effective for CERCLA soils containing both volatile and semivolatile organic compounds.

Working with individual compounds relative to treatment effectiveness is too cumbersome for 17 compounds and elements; therefore, the substances were grouped by class (i.e., volatiles, semivolatiles, and metals). The treatment reductions were calculated for each specific compound/element (in-out), and the individual treatment reduction numbers were summed and averaged to produce one number for each class of compound treated under each different operating condition on each soil.

Volatiles--With the exception of acetone, the data generated by low-temperature thermal desorption indicate that the residual concentration of individual compounds in the soil decreases with increasing temperature. For SARM I, the average treatment efficiencies for temperatures of 150°, 350°, and 550°F were 97.8, 99.8, and 99.8 percent, respectively. Figure 1 plots the overall volatile treatment effectiveness as a function of temperature and shows that treatment effectiveness reaches 99.5 percent and 300°F and then slowly levels off as temperature increases.

The volatiles in SARM II (low organics/low metals) reacted to the thermal treatment in the same manner as SARM I. Acetone, one of the most volatile compounds in the SARM, was not effectively treated by the low-temperature desorption process. The other six volatile compounds, however, responded positively to the treatment with reduction efficiencies of 99.2, 99.8, and 99.9 percent, respectively.

Semivolatiles--The semivolatile organic compounds responded to thermal desorption, but required higher temperatures to generate higher treatment efficiencies. For SARM I the average treatment efficiencies for temperatures of 150°, 350°, and 550°F were 16.8, 53.1, and 94.5, respectively. Figure 2 plots the treatment effectiveness of the semivolatile organic compounds as a function of treatment temperature. It appears that temperatures of 700°F or more are required to achieve treatment effectiveness of 99 percent. The semivolatiles in SARM II displayed the same thermal behavior with treatment efficiencies of 11.7, 74.8, and 86.3 percent reported for the three operating temperatures.

Metals--The data on the metals associated with the synthetic soils were a little different from what was expected. At temperatures of 550°F and

TABLE 2. PEI SOIL THERMAL TREATMENT EXPERIMENTAL SUMMARY

Time at temp = 30 minutes

EXP #	ANALYTICAL SAMPLE #	SAMPLE TYPE	IT SOIL #	EXP TYPE	PURGE RATE	TARGET TEMP	MAX SOIL TEMP	STARTING SOIL WT	TREATED SOIL WT	% WT LOSS	CONDENSED VOLUME
					cc/min	deg F	deg F	g	g		ml
PEI-3	555-12-2A-5416	Soil	5416 f	Tray	90	550	548	72.98	60.59	17.4	nc
PEI-4	555-14-2A-5416	Soil	5416	Tray	90	550	551	73.27	60.20	17.8	nc
PEI-5	555-16-2A-5416	Soil	5416	Tray	90	550	551	74.15	61.18	17.5	nc
PEI-7	555-20-2A-5416	Soil	5416	Tray	90	350	341	75.74	63.08	16.7	nc
(b)	555-20-3A-5416	Soil	5416								
PEI-15	555-38-2A-5416	Soil	5416	Tray	90 a	150	161	74.26	66.99	9.8	nc
PEI-24	555-77-2A-5416	Soil	5416	Tray	90	350	344	105.68	87.06	17.6	nc
PEI-8	555-22-2A-5415	Soil	5415 g	Tray	90	550	550	41.62	39.13	6.0	nc
PEI-9	555-24-2A-5415	Soil	5415	Tray	90	550	550	41.22	38.76	6.0	nc
(c)	555-24-1R-5415	Soil	5415								
PEI-10	555-26-2A-5415	Soil	5415	Tray	90	550	552	41.74	39.25	6.0	nc
PEI-11	555-28-2A-5415	Soil	5415	Tray	90	350	350	41.97	39.85	5.8	nc
PEI-14	555-36-2A-5415	Soil	5415	Tray	90 a	150	152	41.44	39.54	4.6	nc
(d)	555-36-1R-5415	Soil	5415								
PEI-37	561-7-2A-5415	Soil	5415	Tray	90 a	150	147	(e)			

a gas volume exchange rate equivalent of larger furnace to smaller unit rev 01/27/88

b duplicate sample from PEI-7

c duplicate sample from PEI-9

d duplicate sample from PEI-14

e sample from composite runs for TCLP

f IT soil identification number for PEI soil ID SARM-I-1 (high organics/low metals)

g IT soil identification number for PEI soil ID SARM-II-1 (low organics/low metals)

nc not collected

TABLE 3. TRAY TEST RESIDUAL SOIL CONCENTRATION (ppm)

SARM-I-1 (IT05416)

WET WT BASIS Time at temp = 30 minutes

	Goal	Starting soil Conc (ppm) AVG/3 spl	550 F PEI-3	550 F PEI-4	550 F PEI-5	550 F AVG	550 F STD. DEV.	350 F (a) PEI-7	350 F (a) PEI-7	350 F PEI-24	350 F AVG	350 F STD. DEV.	150 F PEI-15
VOLATILES													
ACETONE	6,800	4330	48	160	5.4	71.1	65.20	47	77	58	60.7	12.39	20
CHLOROBENZENE	400	322	(.005	.003	ND0.005	(.004		.065	.059	.052	.059	0.005	13
1,2-DICHLOROETHANE	600	304	ND0.005	.004	ND0.005	(.005		.01	.006	.008	.008	0.0016	ND0.005
ETHYL BENZENE	3,200	3116	.006	.011	.009	.009	0.0021	.48	.41	.39	.43	0.039	130
STYRENE	1000	651	ND0.005	ND0.005	ND0.005	ND0.005		.52	ND0.005	ND0.005	(.18		ND0.005
TETRACHLOROETHYLENE	600	423	ND0.005	(.005	(.005	(.005		.023	.021	.018	.021	0.0021	4.1
XYLENE	8,200	5277	.02	.03	.026	.025	0.0041	.77	.71	1.37	.95	0.30	320
SEMI-VOLATILES													
ANTHRACENE	13,000	7271	(9.4	(19	ND020	(16.1		1300	1600	1177	1359	177.66	5000
BIS(2-ETHYL-HEXYL-)PHTHALATE	5,000	2527	(9.4	ND019	ND020	(16.1		1600	1400	1570	1523	88.07	2100
PENTACHLOROPHENOL	2,000	381	60	75	40	58	14.34	200	230	275	235	30.82	330
METALS													
ARSENIC	10	13.6	15.8	17.4	18.7	17.3	1.19	13.2	12.8	18.9	15.0	2.79	17.8
CADMIUM	20	18.0	24.2	28.3	28.6	27.0	2.01	23.9	25.5	25.5	25.0	0.75	24.6
CHROMIUM	30	22.0	32.1	37.7	38.8	36.2	2.93	32	34.6	30.3	32.3	1.77	31.6
COPPER	190	225	215	260	255	243	20.14	280	309	391	327	47.01	301
LEAD	280	222	280	342	356	326	33.03	280	305	330	308	23.75	298
NICKEL	20	19.8	29.7	34.5	35	33.1	2.39	28.9	30.2	27.5	28.9	1.10	28.9
ZINC	450	431	533	651	670	618	60.60	579	535	731	615	83.97	543
RESIDUAL % MOISTURE		16.89	0	0	0	0		0.75	0.51	1.9	1.05		7.27

a duplicate sample analyses
ND not detected

rev 11/16/87

TABLE 4. TRAY TEST DATA SUMMARY

SARM-II-1 (IT #5415)

TRAY TEST RESIDUAL SOIL CONCENTRATION (ppm)
(WET WT BASIS) Time at temp = 30 minutes

		Starting		550 F					350 F		150 F			
	Goal	Soil Conc (ppm)	PEI-8	(a) PEI-9	(a) PEI-9	PEI-10	AVG	STD. DEV.	PEI-11	(b) PEI-14	(b) PEI-14	PEI-37	AVG	STD. DEV.
VOLATILES														
ACETONE	680	430	67	120	110	100	99.2	19.92	100	6.8	3.1	35	15.0	14.25
CHLOROBENZENE	40	6.6	.006	.004	.004	.004	.004	0.0009	.017	.098	.16	.016	.091	0.059
1,2-DICHLOROETHANE	60	1.3	.012	.008	.005	.007	.008	0.0025	.006	.014	.02	ND0.01	(.015	
ETHYL BENZENE	320	82.5	.044	.034	.034	.03	.035	0.0052	.18	2.5	2.9	.061	1.82	1.25
STYRENE	100	ND0.005	ND0.005	ND0.005	ND0.005	ND0.005	ND0.005		ND0.005	ND0.005	.045	.24	(.097	
TETRACHLOROETHYLENE	60	4.4	.008	.005	.004	.006	.006	0.0015	.009	.028	.045	ND0.01	(.028	
XYLENE	820	155	.14	.097	.074	.089	.1	0.025	.57	4.2	4.7	.343	3.1	1.95
SEMI-VOLATILES														
ANTHRACENE	1300	350	ND@9.8	ND@8.2	(10	ND@9.4	(9.3		23	170	220	324	238	64.15
BIS(2-ETHYL-HEXYL-)PHTHALATE	500	150	ND@9.8	ND@8.2	ND@10	ND@9.4	(9.3		54	170	160	210	180	21.60
PENTACHLOROPHENOL	200	29	ND@9.8	ND@8.2	ND@10	ND@9.4	ND@9.3		(9.5	13	18	36	22.3	9.88
METALS														
ARSENIC	10	14.3	19.4	14.1	20.2	16.1	17.4	2.47	13.1	20	6.9	17.1	14.7	5.62
CADMIUM	20	28.1	31.5	29.8	31.5	29	30.4	1.09	25.9	29.8	24.3	30.8	28.3	2.86
CHROMIUM	30	33.5	46.9	37.1	37.8	33.4	38.8	4.97	31.7	36.1	26.6	31.2	31.3	3.88
COPPER	190	278	323	251	259	231	266	34.45	256	298	231	275	268	27.80
LEAD	280	273	397	297	341	286	330	43.69	289	303	258	299	287	20.34
NICKEL	20	30	33.5	33	34.2	29.5	32.5	1.81	27.6	31.6	24.6	30.1	28.8	3.01
ZINC	450	594	771	706	730	613	705	57.98	563	665	523	601	596	58.07
RESIDUAL % MOISTURE		6.0	12.38(c)	0.87	1.94	2.46	4.41		0	1.93	0	4.73	2.22	

a duplicate sample analyses
b duplicate sample analyses
c see notes on analytical data

rev 01/28/88

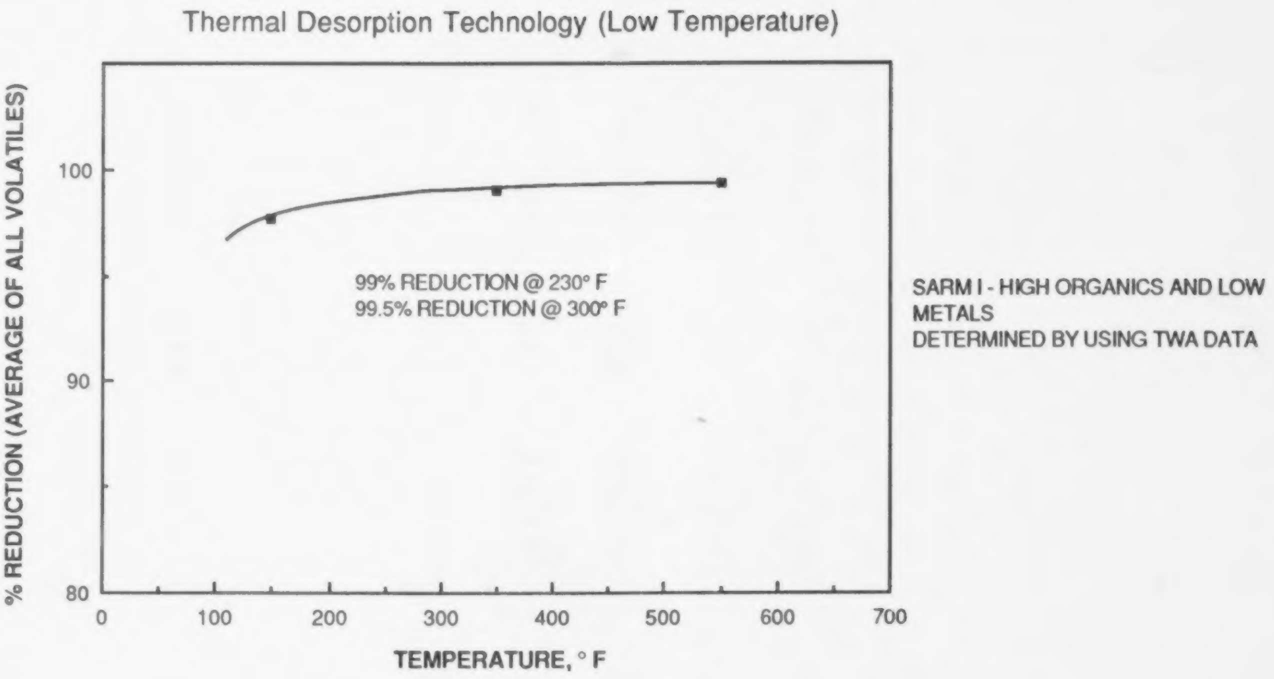


Figure 1. Collection efficiency as a function of temperature for volatiles from SARM I using low temperature thermal desorption.

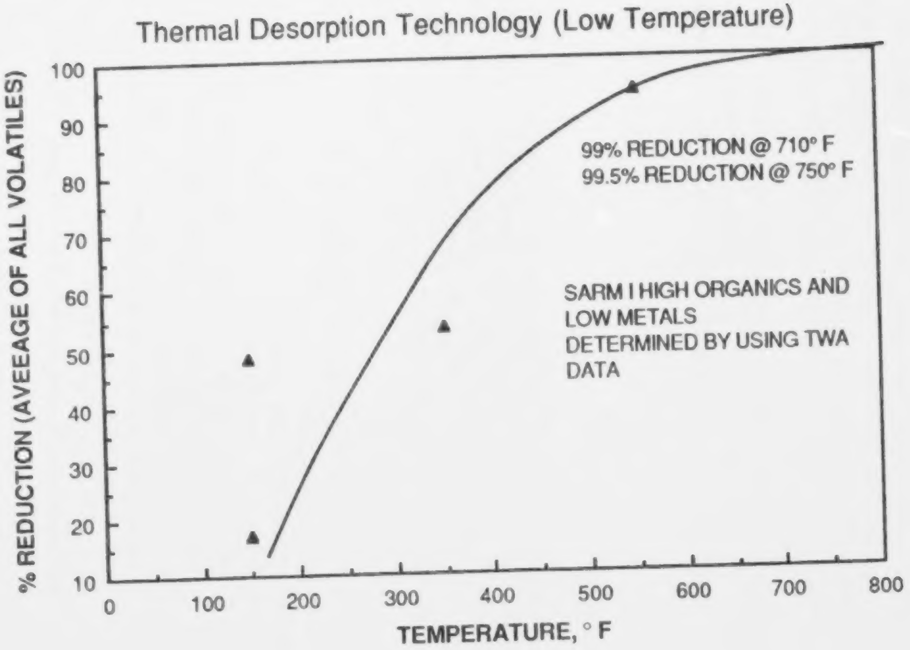


Figure 2. Collection efficiency as a function of temperature for semi-volatiles from SARM I using low temperature thermal desorption.

below, it was expected that the metals would remain in the soil. The data in Table 3 show that a significant amount of each metal was found in the treated soil of SARM I. This trend was not as evident in Table 4 (SARM II) except at the elevated temperatures.

The TCLP analyses were performed on the residues from six tray-furnace runs (150°F, 350°F, and 550°F for both SARMs I and II). These results for SARM I are compared with total waste analyses in Tables 5 and 6. All of the treated soil values (TCLP) for both SARMs I and II are much lower than the total waste analysis values, and the majority of the treated soil values are far below the toxicity characteristic and regulatory value published in the Federal Register[1] for applicable contaminants. The exception to this statement is for the volatile organics at the 150°F level for SARM I; in this case the values are much higher than for the 550°F and 350°F analyses.

For the 150°F SARM I run, chlorobenzene, 1,2-dichloroethane, and tetrachloroethylene exceed regulatory limits. Pentachlorophenol, a semivolatile contaminant, also exceeds the regulatory limit for the 150°F SARM I analysis. Cadmium is the only metal that was higher than its regulatory limit.

Overall, these TCLP results indicate that the synthetic-treated residue, with the exception of a few contaminants in residues treated at the 150°F level, is not very leachable; i.e., most of the contaminants remain bound up with the soil particles.

DISCUSSION AND CONCLUSIONS

It appears from the data on volatiles and semivolatiles that low-temperature thermal desorption could be a useful treatment option for CERCLA soils contaminated with volatile and semivolatile organic compounds. As expected, treatment effectiveness declines with declining temperature, and the best performance in these tests occurred at 550°, followed by the 350°F temperature runs.

It is unknown at this time whether the treatment difficulties experienced with acetone were soil-specific or indicative of all soils containing acetone. The treatment effectiveness appeared to increase as the temperature decreased, and this could be the result of a change in the porosity of the soil. Another possibility for the high-acetone residuals is that the cover lid used for the tray after heating could have had residual acetone after cleaning and this acetone was then condensed by the soil vapors. Future experiments could test this possibility by eliminating the acetone wash from the cycle.

The TCLP analyses performed on the SARMs before and after treatment showed that most of the contaminants were removed to very low levels and the SARMs as a whole are not leachable. In contrast to the treated soil residuals, the TCLP concentrations are mostly uniform across the temperature range with the exception of a few contaminants at 150°F, which were much higher than at the 550° and 350°F levels.

TABLE 5. COMPARISON OF TOTAL WASTE ANALYSIS (UNTREATED SOIL) WITH TCLP RESULTS (TREATED SOIL) FOR SARM II

Analyte	Regulatory level, mg/liter[1]	Concentration, mg/liter			
		SARM II	SARM II	SARM II	SARM II
		Untreated	550°F	350°F	150°F
Volatile Organics					
Acetone	-	430	3.70	2.50	0.40
Chlorobenzene	1.4	6.6	0.10	0.10	0.10
1,2-Dichloroethane	0.4	1.3	0.10	0.10	0.10
Ethyl benzene	-	82.5	0.10	0.10	0.32
Styrene	-	1.31[a]	0.10	0.10	0.10
Tetrachloroethylene	0.1	4.4	0.10	0.10	0.10
Xylenes (total)	-	155	0.10	0.14	0.56
Semivolatile Organics					
Anthracene	-	350	0.01	0.04	0.02
Bis (2-ethylhexyl) phthalate	-	150	0.03	0.06	0.03
Pentachlorophenol	3.6	29	0.04	0.01	0.02
Metals					
Arsenic	5.0	14.3	0.15	0.34	0.15
Cadmium	1.0	28.1	1.34	1.28	1.78
Chromium	5.0	33.5	0.10	0.06	0.10
Copper	-	278	2.19	3.22	7.33
Lead	5.0	273	1.57	2.08	3.73
Nickel	-	30	0.94	0.90	1.51
Zinc	-	544	26.60	27.30	35.6

[a] From TCLP analysis of untreated soil for SARM II.

TABLE 6. COMPARISON OF TOTAL WASTE ANALYSIS (UNTREATED SOIL) WITH TCLP RESULTS (TREATED SOIL) FOR SARM I

Analyte	Regulatory level, mg/liter[1]	Concentration, mg/liter			
		SARM I	SARM I	SARM I	SARM I
Volatile Organics		Untreated	550°F	350°F	150°F
Acetone	-	4330	1.0	1.93	20.00
Chlorobenzene	1.4	322	0.10	0.10	2.89
1,2-Dichloroethane	0.4	304	0.10	0.10	0.43
Ethyl benzene	-	3116	0.10	0.10	44.00
Styrene	-	651	0.10	0.10	3.08
Tetrachloroethylene	0.1	423	0.10	0.10	1.28
Xylenes (total)	-	5277	0.10	0.11	55.10
Semivolatile Organics					
Anthracene	-	7271	0.01	0.86	0.02
Bis (2-ethylhexyl) phthalate	-	2527	0.03	0.78	0.16
Pentachlorophenol	3.6	381	0.35	5.27	1.61
Metals					
Arsenic	5.0	13.6	0.15	0.15	0.15
Cadmium	1.0	18.0	0.88	1.14	1.28
Chromium	5.0	22.0	0.04	0.13	0.10
Copper	-	225	0.38	5.13	6.80
Lead	5.0	222	0.24	2.26	2.84
Nickel	-	19.8	0.58	1.08	1.36
Zinc	-	431	13.80	24.00	27.30

The volatiles distilled off by the low-temperature desorption process would need to be treated, reclaimed, or recycled. If the residue soil contained metals, the soil would also need additional treatment, such as solidification. Both of these factors will add significant costs to a project, but these costs were not factored into the evaluation of the technology for low-temperature thermal desorption.

REFERENCES

1. Federal Register, Vol 51, No. 114, Friday, June 13, 1986/Proposed Rules.

EVALUATION OF SOLIDIFICATION/STABILIZATION AS A BEST DEMONSTRATED AVAILABLE TECHNOLOGY

by

Leo Weitzman and Lawrence E. Hamel
Acurex Corporation
Research Triangle Park, NC

and

Edwin Barth
Hazardous Waste Engineering Research Laboratory, U.S. EPA
Cincinnati, OH

ABSTRACT

This project evaluated the performance of solidification as a means of treating soil from "Superfund" sites. Tests were conducted on four different types of artificially contaminated soil which are representative of the types of contaminated soils found at Superfund sites. The soils were solidified using the following three commonly used solidification agents or binders: (1) portland cement, (2) lime kiln dust, and (3) a mixture of lime and flyash.

At 7, 14, 21, and 28 days after soil and binders were mixed, samples of the solidified material were subjected to Unconfined Compressibility (UCS) testing. Samples of those mixes that had a UCS minimally greater than 50 psi (pounds per square inch), or which showed the highest UCS below 50 psi, after 14 and 28 days were subjected to Toxic Contaminants Leaching Procedure (TCLP) and Total Waste analysis (TWA). The 50-psi level was chosen based on guidance from the Office of Solid Waste and Emergency Response (OSWER directive No. 9437.00-2A). The principal goal of this program was development of screening data in support of the Office of Environmental Emergency Response (OEER). The schedule and experimental protocol were therefore geared to satisfying these regulatory demands.

As an ancillary goal, the results were analyzed to determine if any correlations could be obtained between the degree of toxicant immobilization, as determined by the TCLP, and the following other parameters: (1) UCS results, (2) curing time, (3) contaminant level, (4) binder type, and (5) water concentration.

The impact of these parameters on the leachability of the contaminants is complex. It was recognized at the start of the testing that this

abbreviated set of experiments was not likely to adequately address these interactions. For completeness, however, these correlations were attempted.

The following results were observed:

1. The water-to-total-solids ratio appears to be a better measure of the amount of water needed to solidify a given mix than the water-to-binder ratio that is commonly used. This was clearly the case for the "Synthetic Analytical Reference Matrix" (SARM) with these binders. This needs to be confirmed on other systems.

2. Solidifying the SARM resulted in significant reductions in the amount of metal salt contaminants released, as measured by the TCLP.

3. Solidification did not appear to result in a similar reduction in the amount of organic emissions from the SARM. Because of the large losses of organics during the mixing process, the effect of solidification on the organic leachate via the TCLP could not be determined. The volatile and semivolatile organic contaminants did appear to decrease during the solidification process; however, this decrease can be attributed to their release to the air during processing and curing.

4. No correlation between UCS and the results of the leaching tests was observed.

This work was performed under Contract No. 68-03-3241, Work Assignment No. 2-18 from the EPA. This paper has not been subjected to agency peer review. The contents do not necessarily reflect the views and policies of the U.S. Environmental Protection Agency, nor does mention of trade names or commercial products constitute endorsement or recommendation of use.

The Hazardous Solid Waste Amendment Act (HSWA) of 1984 requires the U.S. Environmental Protection Agency (EPA) to develop treatment standards or treatment methods (called "Best Demonstrated Available Technology" or "BDAT") for listed hazardous waste before it is land disposed. Treatment methods are to be developed which reduce the toxicity or the likelihood of the migration of the hazardous constituents in the waste. The Superfund Amendment and Reauthorization Act (SARA or Superfund) requires that remedial actions meet all applicable, relevant, and appropriate public health and environmental standards. Therefore, the Superfund program must be consistent with the BDAT approach when disposing of contaminated soils and debris from Superfund sites.

In order to satisfy this requirement, it is necessary to establish the level of performance (as determined by the above criteria) that different technologies can achieve on materials from Superfund sites. The Office of Research and Development (ORD) assisted the Office of Environmental and Emergency Response (OEER) in evaluating five technologies which could be the BDAT for soil and debris from Superfund sites. The five technologies were

1. incineration
2. low temperature thermal desorption
3. KPEG reagent for dechlorination
4. aqueous soil washing
5. solidification/stabilization

This project evaluated the performance of solidification/stabilization as a "BDAT" for treating soil from "Superfund" sites. Prior to starting the discussion, it is necessary to define solidification and stabilization. Solidification is a treatment process whereby a waste is converted into a solid material that does not flow and which will support a load. Stabilization is a process that results in the reduced mobility of the contaminants in a waste or other material. Stabilization may be accompanied by the solidification of a waste and, as a result, the terms are often interchangeable; however, they do denote different phenomena.

For this program, four different types of artificially contaminated soil, which are representative of the types of contaminated soils found at Superfund sites, were solidified using three commonly used solidification agents or binders. The products were subjected to Unconfined Compressibility (UCS) tests, and each blend of soil and binder which had a UCS minimally greater than 50 psi (pounds per square inch), or which showed the highest UCS below 50 psi after curing, were subjected to Toxicity Characteristic Leaching Procedure (TCLP) and Total Waste Analysis (TWA) to determine the performance of this type of solidification as a possible pretreatment method for contaminated soils from Superfund sites. The 50-psi criterion is consistent with Resource Conservation and Recovery Act (RCRA) listed waste regulations.

The binders used were commonly available generic agents which are readily available. Other binders, both proprietary and generic, are available and could enhance the stabilization process. There is, at present, no set protocol for evaluating the efficacy of stabilization technologies.

The TCLP was used for evaluating the level of stabilization achieved in this program. It is one of several leaching procedures commonly used at present.

EXPERIMENTAL PROCEDURE

The "soils" used for this evaluation are identified as the "Synthetic Analytical Reference Matrix" (SARM) and defined as SARM 1 through SARM 4. The SARM's were prepared for EPA under a separate program and are described in Reference (1). They are identified as:

- SARM I -- low metals, high organics concentration
- SARM II -- low metals, low organics concentration
- SARM III -- high metals, low organics concentration
- SARM IV -- high metals, high organics concentration

Upon receipt, each SARM was subjected to a total waste analysis (TWA) for the specified metal and organic contaminants that had been added to it in its preparation. Table 1 gives the results of this analysis. By way of comparison, Table 2 shows the results of the multiple TWA analyses on the SARM's immediately after preparation. This information was obtained from Reference (1), which describes the SARM's and the procedures used to prepare them. The actual metal salts used to contaminate the SARM's are listed in Table 3. The three binders used were portland cement, Type 1 (PC); lime kiln dust (KD); and equal weights of technical grade lime and flyash (LF).

TABLE 3. CHEMICAL IDENTIFICATION AND SOLUBILITY
OF SARM METAL CONTAMINANTS

Chemical Type	Solubility in Water
Lead sulfate ($PbSO_4$)	Slightly soluble
Zinc oxide	Insoluble
Cadmium sulfate ($3CdSO_4\ 8H_2O$)	Soluble
Arsenic trioxide (As_2O_3)	Slightly soluble
Copper sulfate ($CuSO_4\ 5H_2O$)	Soluble
Chromic oxide (Cr_2O_3)	Insoluble
Nickel nitrate ($Ni[NO_3]_2$)	Soluble to very soluble

The portland cement was standard Type 1 portland cement manufactured by the W. R. Bonsal Company of Charlotte, NC. It was identified as meeting ASTM specification C-150 and Federal Specification SS-C-1960-3A for Type 1 and 2. The lime kiln dust was obtained from the Mississippi Lime Company's Ste. Genevieve, Missouri, plant. The lime was hydrated agricultural lime manufactured by the Tennessee Lime Division of Tenn Luttrell Company, Luttrell, Tennessee. The flyash was a nonpozzolanic flyash obtained from a local power plant.

TABLE 1. RESULTS OF TWA FOR SARM SAMPLES RECEIVED FOR THIS PROGRAM

(mg/kg)

Analyte	SARM 1 High organic, low metal	SARM 2 Low organic, low metal	SARM 3 Low organic, high metal	SARM 4 High organic, high metals
Volatiles				
Acetone	3,150	230	220	13,000
Chlorobenzene	330	9.2	8.9	270
1,2-dichloroethane	380	3.9	3.1	830
Ethylbenzene	3,350	74	100	2,500
Styrene	1,000	26	24	540
Tetrachloroethylene	710	16	13	540
Xylene	4,150	210	150	3,700
Semivolatiles				
Anthracene	940	275	265	775
Bis(2-ethylhexyl) phthalate	600	34	140	500
Pentachlorphenol	135	62	15	78
Inorganics				
Arsenic	18	18	904	810
Cadmium	17	23	1,280	1,430
Chromium	27	37	1,190	1,650
Copper	193	260	9,650	13,300
Lead	190	240	15,200	16,900
Nickel	27	32	1,140	1,380
Zinc	392	544	53,400	28,900

TABLE 2. RESULTS OF TWA FOR SARMS IMMEDIATELY AFTER MIXING(1)
(mg/kg)

(As determined by PEI from main blend prior to shipping samples)

Analyte	SARM 1 High organic, low metal	SARM 2 Low organic, low metal	SARM 3 Low organic, high metal	SARM 4 High organic, high metals
Volatiles				
Acetone	4,500 (7)	360 (8)	360 (2)	8,030 (2)
Chlorobenzene	320 (7)	13 (6)	11 (2)	330 (2)
1,2-dichloroethane	380 (7)	7 (8)	5 (2)	490 (2)
Ethylbenzene	3,460 (7)	120 (8)	140 (2)	2,710 (2)
Styrene	730 (7)	48 (7)	32 (2)	630 (2)
Tetrachloroethylene	480 (6)	19 (8)	20 (2)	900 (2)
Xylene	5,720 (7)	210 (8)	320 (2)	5,580 (2)
Semivolatiles				
Anthracene	4,390 (7)	350 (7)	270 (3)	1,920 (3)
Bis(2-ethylhexyl) phthalate	1,830 (7)	140 (6)	270 (3)	1,920 (3)
Pentachlorphenol	270 (5)	40 (4)	30 (3)	80 (3)
Inorganics				
Arsenic	21 (8)	18 (7)	690 (4)	540 (4)
Cadmium	27 (6)	32 (6)	2,380 (2)	3,790 (2)
Chromium	30 (6)	32 (6)	1,260 (4)	1,400 (4)
Copper	260 (8)	280 (8)	9,550 (4)	11,250 (4)
Lead	270 (8)	320 (8)	15,100 (4)	15,680 (4)
Nickel	39 (8)	40 (8)	1,540 (4)	1,550 (4)
Zinc	570 (6)	680 (8)	34,450 (4)	28,660 (4)

Note: Values in parentheses indicate number of samples analyzed

In the first step, the water content of the SARM's was determined by drying them to constant weight and attributing the weight loss to water removed by evaporation. The results are given in Table 4. This measurement includes volatile compounds other than water; however, the error introduced by this is insignificant for the purpose of this program.

TABLE 4. WATER CONTENT OF SARM SOILS

SARM	Apparent Water Content, %
1	31.4
2	8.6
3	19.3
4	22.1

The next step of the program was to determine the amount of water required to form a satisfactory product. This was done in two stages. The first stage was a preliminary series of tests conducted to get the general range and the second stage was a finer set of tests to identify the approximate "optimum" amount of water needed to achieve solidification. The "optimum" was defined for this test to be that mix which gave the product most resistant to penetration by a U.S. Army Corps of Engineers, Cone Penetrometer test after 24 h.

More than 600 samples were mixed as part of these tests to identify the amount of water needed to achieve "optimum" conditions. Unfortunately, because of regulatory time constraints, the "optimum" had to be determined on the basis of only one day of curing rather than on longer cure times that would be common in normal operations.

The tests were conducted by mixing each SARM and binder combination with different amounts of water. Each sample was then molded into a plastic cup and allowed to cure for 24 h. At that time, the sample was tested, using a U.S. Army Corps of Engineers Cone Penetrometer, to determine how much it had set up. The preliminary screening resulted in identifying the minimum amount of each binder that was needed to solidify each SARM. The second set of these tests identified the "optimum" amount of water that resulted in the strongest product for each SARM-binder combination.

The tests showed two things. First, they showed that water-to-binder ratios were not good indicators of the amount of water that should be used to form the SARM's into a monolithic solid suitable for hardness testing. The ability of the product to set up could be correlated reasonably well to the water-to-total-solids ratio (W/TS) of the mix. This ratio is simply the mass of water used versus the sum of the solid component of the SARM and of the solidifying agent. In virtually all cases tested, a W/TS ratio of 0.4 to 0.5 resulted in an acceptable product. The second fact which became evident was that regardless of the soil or the binder used, a W/TS ratio of approximately 0.4 resulted in indications of solidification of the material.

The next phase of the program was intended to determine the minimum binder-to-soil (B/S) ratio which would result in a sample of solidified soil with an unconfined compressibility greater than 50 psi. Actually, with some binders this UCS level could not be achieved with any ratio tested within the 30-day curing time set under this program. In that case, the sample that achieved the highest UCS level was used for subsequent testing.

The B/S ratio tests were performed by mixing each soil (4 soils) with each binder (3 binders) at three B/S ratios. Each day, one SARM was mixed with one binder at the three B/S ratios. Table 5 shows how this was performed. Six samples of each mixture constituted one complete set. From each set, four were molded into cubes. Three of these were used for one set of UCS tests, conducted in triplicate, and the fourth as a spare. The fifth was placed in several glass jars with Teflon lined lids and was sent to the laboratories for TCLP and total waste analyses. The sixth set of samples was stored for future reference.

On the seventh day after mixing the SARM with the binders, Set 1 of each sample was subjected to UCS testing. On the 14th day, Set 2 was similarly tested in triplicate. The same was done with Sets 3 and 4 on the 21st and 28th days, respectively. On the 14th and 28th days, the laboratories conducting the UCS and TCLP tests were called and asked which of the samples had either minimally satisfied the 50-psi UCS requirement or, if none had achieved 50 psi, which one had the highest UCS reading. The program resulted in a total of 648 samples, as shown below:

4 Soil types
x 3 Binders
x 3 B/S ratios
x 3 Triplicate samples
x 6 samples at each condition
648 Total samples

The samples that were used for UCS testing were molded according to the specifications in ASTM C 109-86. The procedure calls for molding the material in specially fabricated stainless steel or brass molds which result in cubes two inches (5.08 cm) long on each side. The molds must meet strict dimensional and stiffness requirements. The resulting samples were allowed to harden for one to four days at 70 °F (±10 °F) and 90 to 100% humidity, then unmolded, and each cube was placed in a sealable plastic bag to cure at room temperature until it was tested. Table 5 also gives the ratios of each component (SARM, binder, and water) in each sample and summarizes the results of the UCS tests.

In a few cases, different B/S ratios satisfied the UCS criteria at the 14th and 28th days. For example, Sample 30 satisfied the UCS criteria after 14 days of curing while Sample 29 satisfied them after 28 days. This happened with several mixtures.

TABLE 5. MIX RATIOS AND RESULTS OF UCS TESTS FOR EACH SAMPLE SET, SUMMARY

Sample Number	SARM Type	Binder Type	B/S Ratio	W/TS Ratio	Days After Mixing 7	14	21	28
1	I	PORTLAND	0.7	0.40	NA	977	NA	1093
2	I	CEMENT	1.2	0.40	NA	>1000	NA	>1000
3	I	TYPE 1	2.3	0.40	NA	>1000	NA	>1000
4	II	PORTLAND	0.7	0.40	NA	>1000	NA	>1000
5	II	CEMENT	1.2	0.40	NA	>1000	NA	>1000
6	II	TYPE 1	2.3	0.40	NA	>1000	NA	>1000
7	III	PORTLAND	0.7	0.40	NA	28	NA	>1000
8	III	CEMENT	1.2	0.40	NA	99	NA	>1000
9	III	TYPE 1	2.3	0.40	NA	71	NA	>1000
10	IV	PORTLAND	0.7	0.40	NA	15.8	NA	16.2
11	IV	CEMENT	1.2	0.40	NA	167	NA	160
12	IV	TYPE 1	2.3	0.40	NA	177	NA	300
13	I	KILN	1	0.40	5	72.9	93	113
14	I	DUST	2	0.45	5	51.8	54	241
15	I		3	0.40	176	211	215	81.1
16	II	KILN	1	0.40	37.5	59.7	78.3	85.1
17	II	DUST	2	0.40	128	190	164	216
18	II		3	0.40	183	225	275	252
19	III	KILN	1	0.40	32.9	36.6	37.1	38.5
20	III	DUST	2	0.40	33	38.4	40.8	39
21	III		3	0.40	45.7	44.7	43.7	79.8
22	IV	KILN	1	0.42	27.9	28.1	26.8	32.2
23	IV	DUST	2	0.43	38.9	55.7	52.4	52.2
24	IV		3	0.40	35.7	38.2	33	40.1
25	I	LIME/	1	0.45	24.1	27.3	26	32.3
26	I	FLYASH	2	0.45	22.2	29	33.9	40.4
27	I		3	0.45	19.5	30.4	32.9	46.6
28	II	LIME/	1	0.45	9.9	17.1	17.3	28.8
29	II	FLYASH	2	0.48	17.2	24.2	26.9	62.4
30	II		3	0.49	19.4	31.4	41.2	73.4
31	III	LIME/	1	0.48	21.9	28.7	29.1	30.7
32	III	FLYASH	2	0.49	30.3	33	36.4	36.5
33	III		3	0.50	34.8	48.8	48.2	50.9
34	IV	LIME/	1	0.45	34.9	36	34.8	37.9
35	IV	FLYASH	2	0.40	29.8	38.7	36.3	40.5
36	IV		3	0.45	36.9	35.7	37.9	42.2

The organic volatile and semivolatile emissions from the solidified samples were qualitatively measured to track the loss of organic components from the samples into the surrounding air. After curing overnight in the molds, the SARM samples were placed into polyethylene bags and sealed. At 14 and 28 days, a five-milliliter sample of the air in the bag of the SARM sample was withdrawn for analysis before the bag was opened and the cube measured.

It should be noted that this methodology only gave the concentration of the compounds in the headspace. Because no gas flux measurements through the plastic bags were made, these concentrations cannot be used to calculate the emission rate of the organics. Because of this limitation of the experiment, they should be construed as qualitative in nature.

The TCLP analyses were performed for both organics and metals; however, because of the significant losses of the organic constituents during mixing and handling, the results of the TCLP analyses proved inconclusive. As a result, they are not presented here. This observation is discussed further below. The results of the TCLP analyses for metals are presented in Table 6.

Table 6 lists the SARM type (I through IV) and the sample number that was tested in the first column. The second column identifies the type of binder used. "RAW" is the contaminated SARM without stabilization and PC, KD, and LF are the three binders. The numbers in parenthesis identify the day the analyses were performed--14 or 28 days after mixing. The final columns present the TCLP results for each metal: (a) giving the parts per million (ppm) of that metal found in the extract, and (b) giving the percent decrease that this represents over the raw SARM. It should be noted that the values in the (b) column correct for the decrease in the concentration of that metal that is due to dilution by the binders. For example, if the binder-to-soil ratio was 1:1, then normal dilution would result in a halving of the TCLP. The percent reduction corrects for this dilution effect.

Table 7 gives the results of the TWA analyses for the metals in both the raw and solidified SARM's. The data is presented in a similar format as in Table 6, except that the results are only presented as parts per million of each metal in the product. Because TWA is only an indication of the amount of each component present in the sample, the results are not corrected for dilution in Table 7. The final report does present the results corrected for dilution.

DISCUSSION OF RESULTS AND CONCLUSIONS

The results indicated that the portland cement formed a much stronger matrix than the other two binders. Typically, the portland cement resulted in a UCS exceeding 1000 psi (the upper limit of measurement with the available equipment) for three out of the four SARM's. Further, it achieved these levels at far lower soil-to-binder ratios than the other two binders, resulting in a smaller volume of waste requiring ultimate disposal. The strength of the product solidified with portland cement was significantly lower for SARM IV than for the other three SARM's. The SARM IV had been contaminated with very high levels of both organic compounds and metal salts

TABLE 6. SUMMARY OF TCLP RESULTS FOR METALS

(SARM) Sample No.	Binder (Day)	Arsenic a	Arsenic b	Cadmium a	Cadmium b	Chromium a	Chromium b	Copper a	Copper b	Lead a	Lead b	Nickel a	Nickel b	Zinc a	Zinc b
I	RAW	ND		0.53		ND		0.61		0.49		0.27		9.2	
1	PC(14)	ND	–	ND	100	0.06	+	0.07	81	0.15	75	0.04	70	0.23	96
14	KD(14)	ND	–	ND	100	0.06	+	0.04	81	ND	100	ND	100	0.27	94
27	LF(14)	ND	–	ND	100	0.02	+	0.03	98	ND	100	ND	100	0.14	94
1	PC(28)	ND	–	ND	100	0.06	+	0.06	83	0.15	75	0.04	70	0.49	91
15	KD(28)	ND	–	ND	100	0.09	+	0.03	80	ND	100	ND	100	0.62	73
27	LF(28)	ND	–	ND	100	0.02	+	0.03	98	ND	100	ND	100	ND	100
II	RAW	ND		0.73		ND		0.89		0.7		0.4		14.6	
4	PC(14)	ND	–	ND	100	0.03	+	0.04	92	0.15	82	0.04	83	0.09	99
16	KD(14)	ND	–	ND	100	0.08	+	0.07	79	0.44	+	ND	100	0.25	97
30	LF(14)	ND	–	ND	100	ND	–	ND	100	ND	100	ND	100	0.22	99
4	PC(28)	ND	–	ND	100	0.03	+	0.06	89	0.15	83	0.04	83	0.54	94
16	KD(28)	ND	–	ND	100	0.05	+	0.09	89	0.37	+	ND	100	0.78	89
29	LF(28)	ND		ND	100	ND	–	0.03	90	ND	100	ND	100	0.02	100
III	RAW	6.39		33.1		ND		80.7		19.9		17.5		359	
7	PC(14)	ND	–	ND		0.07	+	0.15	100	0.63	95	ND	100	0.58	100
21	KD(14)	ND	–	ND	100	0.22	+	1.02	96	13.3	+	ND	100	4.38	95
33	LF(14)	0.81	52	0.02	100	0.03	+	2.96	87	51	+	ND	100	3.81	96
7	PC(28)	ND	–	ND	100	0.07	+	0.09	100	ND	100	ND	100	0.69	100
21	KD(28)	0.21	98	ND	100	0.12	+	0.85	96	18.3	+	ND	100	4.07	95
33	LF(28)	0.79	51	0.02	100	0.07	+	2.59	87	51	+	0.03	99	3.97	96
IV	RAW	9.58		35.3		0.06		10		70.4		26.8		396	
10	PC(14)	ND	100	ND	100	0.06	+	0.14	100	0.39	99	ND	100	0.39	100
23	KD(14)	0.16	95	ND	100	0.11	+	1.88	97	12.4	43	ND	100	4.57	97
	LF(14)	1.61	50	ND	100	0.07	+	1.92	96	91.8	+	ND	100	3.22	96
10	PC(28)	ND	100	ND	100	0.06	+	0.17	100	0.37	99	ND	100	0.74	100
23	KD(28)	0.27	92	ND	100	0.12	+	1.67	97	21.4	9	ND	100	3.72	97
	LF(28)	0.98	59	0.02	100	0.07	+	2.18	95	65	+	ND	100	3.64	96
Detection Limit		0.15		0.01		0.01		0.02		0.15		0.04		0.01	

Notes: (a) TCLP results in ppm
(b) percent reduction, corrected for dilution

ND - below detection limit
+ - increase over raw SARM

TABLE 7. SUMMARY OF TWA RESULTS, METALS

(SARM) Sample No.	Binder (Day)	TWA Results (ppm)						
		As	Cd	Cr	Cu	Pb	Ni	Zn
I	RAW	18	17	27	193	190	27	392
1	PC(14)	18	18	49	195	453	37	393
14	KD(14)	15	12	31	113	183	65	299
27	LF(14)	29	8	14	78	89	19	182
1	PC(28)	15	17	56	164	189	32	320
15	KD(28)	12	12	22	101	119	69	232
27	LF(28)	30	9	19	62	113	16	151
II	RAW	18	23	37	260	240	32	544
4	PC(14)	15	18	47	125	149	34	351
16	KD(14)	14	17	51	133	280	50	383
30	LF(14)	28	10	15	85	97	21	161
4	PC(28)	23	24	45	218	294	39	479
16	KD(28)	15	20	27	153	193	53	404
29	LF(28)	32	11	19	106	134	20	276
III	RAW	904	1,280	1,190	9,650	15,200	1,140	53,400
7	PC(14)	528	797	1,010	6,390	11,600	625	14,800
21	KD(14)	223	315	391	2,420	4,710	300	7,600
33	LF(14)	196	258	299	1,810	3,830	216	5,850
7	PC(28)	584	934	1,060	7,960	12,100	724	22,200
21	KD(28)	233	326	432	2,660	4,390	300	7,690
33	LF(28)	180	251	279	1,660	2,780	169	4,830
IV	RAW	810	1,430	1,650	13,300	19,900	1,380	28,900
10	PC(14)	506	858	1,060	7,040	12,100	616	17,500
23	KD(14)	290	541	550	4,230	6,320	418	11,200
35	LF(14)	281	448	461	4,440	6,590	374	9,890
10	PC(28)	563	952	1,020	10,100	8,680	753	21,000
23	KD(28)	271	490	516	4,860	5,190	449	12,300
36	LF(28)	225	306	386	3,430	4,590	255	7,020

and it appears that this combination resulted in a large amount of interference to the solidification process.

The lime kiln dust and the lime/flyash mixtures used for these tests did not result in values of the UCS as high as those observed with portland cement--even for SARM IV. The samples solidified with these binders were generally very weak. The strength (UCS), however, continued to increase during the course of these tests. The trend in the data was very clear and confirmed the general impression that lime-based binders will continue to harden over time.

The SARM samples stabilized with lime and lime kiln dust/flyash continued to cure over time. The UCS values for these samples started very low but as time progressed, they increased. The test suggests that the curing time for these binders should have been extended to determine their ultimate strength. The trend in the data suggested that these samples would continue to show increases in their UCS beyond the 30-day period.

An observation made during the initial screening tests of this program appears to be useful for further work. These tests showed that a water/solids ratio of approximately 0.4 would result in a solidified product regardless of the binder used--within the overall context of the experiment. This observation, if confirmed with other systems, could result in a significant reduction in the number of experiments required to test a given waste/binder ratio.

The results of the TCLP for the metals on the treated SARM's was very encouraging. The data show that the metals leaching from the SARM's are reduced significantly by the solidification process. In fact, the reduction approached 100% for many of the compounds. Many of the metal salts appeared to be attenuated by the SARM itself.

The TCLP results on the raw (unsolidified) contaminated SARM's were lower than the expected values for almost all of the metals. This made the data difficult to interpret as many of the analyses were being made at or near the detection limits. Nevertheless, the results clearly indicate a significant reduction in the TCLP of each of the metals in almost all cases.

It should be emphasized that the unsolidified SARM's themselves proved to be reasonably good stabilizing agents. Examination of the TCLP results of the raw SARM's showed that the matrix itself prevented a large portion of the metals from being released to the TCLP. Many analyses of the raw, contaminated material approached the minimum level of sensitivity of the analyses.

All of the binders reduced the leachability of the cadmium, copper, nickel, and zinc. In all of these cases, the solidified SARM's resulted in only trace amounts or less of these metal salts in the leachate. The TCLP results for lead was less consistent. All of the samples that were solidified with portland cement showed very large reductions in the leachability of this ion. The kiln dust showed some reduction in the leachability of the lead, although the reduction was not as great as for the portland cement.

The lime/flyash binder showed no apparent reduction in the leachability of the lead. In fact, the results actually showed an increase in the leachability after correcting for dilution. The increase is most likely due to the error introduced by the large amount of binder used for these samples and the resultant large dilution factor, rather than being an actual increase. However, the results clearly showed no apparent reduction in the leachability of lead with this binder.

The arsenic was stabilized well by the portland cement and the kiln dust. The lime/flyash binder also reduced the arsenic's leachability, but only by approximately 50%.

The solidification process had virtually no effect on the chromium ion in this program. In fact, as with the lead solidified by the lime/flyash mix, the concentration of chromium in the leachate appeared to increase after correcting the results of the TCLP on the solidified material for dilution. Once again, this increase is most likely an artifact of the experiment; however, it is reasonably certain that this solidification did not reduce the leachability of the chromium ion.

The reason for the negative results on the chromium and (to a lesser extent) the lead with lime/flyash is uncertain. Table 7 lists the actual metal salts that were used to spike the SARM's and their solubilities in water. As can be seen, the solubility of the salts does not appear to be a factor. Chromic oxide is insoluble and so is zinc oxide, yet the zinc was fixed and the chromium was not. Similarly, both the lead and arsenic salts used are slightly soluble, yet they also behaved differently.

The metal oxides (represented here by zinc, arsenic, and chromium) are generally inert. The calcium oxide and hydroxide in the binders are not likely to react with them. Conceivably, the calcium hydroxide in the lime-based binders could react with sulfates or nitrates--represented here by the salts of lead, cadmium, copper, and nickel; however, here again the results were not consistent enough to draw a conclusion. Further research into the chemical mechanisms involved in the solidification process is needed to correlate these observations.

Another observation of the TCLP data was that the results for each sample at 14 days was the same (to within sampling and analytical error) as that for the same sample at 28 days. If this correlation could be confirmed, significant reductions in the time required for such testing could be realized. This result is also of interest because it indicates that, at least for the lime/flyash and the lime kiln dust, the UCS is not a good indicator of how well metals are immobilized. The UCS of the samples formed with these binders continued to increase even though there was little change in the TCLP.

The TWA results for the metals appeared inconsistent. Some of the metals showed large increases in concentration and some, decreases. Once again, the problem is most likely in the "leveraging" of any error by the dilution correction.

The variability due to the analytical method can be estimated by examining the difference between the TWA for the metals for each mix after 14 and 28 days. For example, SARM III solidified with portland cement (PC) after 14 days (Sample 7) showed 528-ppm arsenic. The same sample at 28 days showed 584 ppm. Generally, comparison of the metals analyses for each sample at 14 and 28 days showed a similar consistency. This type of variability is quite small, indicating that the mixing procedures used in this program resulted in a homogeneous product and that the analytical protocol appeared to give reasonably consistent results.

The analysis of the volatile and semivolatile organic compounds in the headspace by gas chromatography/flame ion detector (GC/FID) seemed to indicate that the emissions dropped only slightly from 14 days to 28 days. This is consistent with other research done by Acurex (EPA Contract No. 68-02-3993, W.A. 32 and 37) which showed that volatile organic emissions occur mostly during mixing, and then continue at a steady rate after curing in a stabilized sample, dropping as the organic content of the solidified material is reduced.

The solidified SARM's generally showed a lower TCLP value for the volatile organic contaminants than the original SARM's. This cannot, however, be attributed to the solidification process binding the volatile compounds so that they are not accessible. Rather, this is most likely due to a simple release of the volatile compounds during the mixing process and during the sample preparation prior to extraction. This was corroborated by other research (2). Because of this fact, the TCLP results for the volatile organics are not considered to be significant and are not presented in this paper. They are presented in the final report for this program.

The TCLP for the semivolatile organics, in general, showed a significant decrease because of solidification. The results show that the percent decrease in the TCLP analyses for the semivolatile organics is greatest for SARM's I and IV (those contaminated with high levels or organics) and least for II and III. SARM's II and III also show a greater variability for the semivolatile reduction, but this is most likely due to analytical errors caused by the low concentration of the semivolatile compounds.

The TWA analyses for the volatile organics showed the same pattern as the TCLP. The TWA analyses, however, showed the results magnified. That is, the solidified SARM's contained on the order of 80 to 90% less volatile organics than the original material. This is consistent with the hypothesis that the volatile organics were released to the air rather than trapped in the solid. Had the volatile organics truly been solidified, then the TWA would have shown a constant value for these materials while the TCLP would have shown a decrease.

The TWA results for the semivolatile organics was unexpected. Stabilization appeared to result in an apparent increase in almost all of the values. This is most likely an artifact of the analytical method. The TWA results appear to have a very wide variation in them. The reason for this is unclear, but it may be due to the physical nature of the semivolatile compounds. They are heavy solids that go into solution slowly. As a result, the amount of each constituent in the liquid after the extraction for analysis may be more of a function of how much of the material actually dissolves than of the total amount of that compound in the waste. Under normal conditions, this error is not significant; however, in this case, the TWA values are corrected for dilution. This results in a "leveraging" of any error and a much higher degree of uncertainty for the TWA results.

In conclusion, it appears that solidification can reduce the leachability of many metals to near zero. Even in this case, when no effort was made to match the solidification process to the contaminant, most of the contaminants were effectively immobilized as determined by the TCLP. It is likely that with a proper choice of binder, it should be possible to immobilize other inorganic contaminants and, possibly, even some of the organics.

REFERENCES

1. Locke, B.B., Esposito, P.M., Furman, C., and Traver, R. P. CERCLA BDAT standard analytical reference matrix (SARM) preparation and results of physical soils washing experiment. Draft Paper.

2. Weitzman, L., Hamel, L. and Cadmus, S. Volatile organic emissions from stabilized hazardous wastes. Final Report, EPA Contract #68-02-3994, WA 32 and 37, August, 1987.

SITE DEMONSTRATION OF SHIRCO INFRARED INCINERATOR

by

Howard O. Wall
Thermal Destruction Branch
Hazardous Waste Engineering Research Laboratory, EPA

and

Seymour Rosenthal
Technology Manager
Enviresponse, Incorporated

ABSTRACT

A Shirco Infrared System used for a removal action at a PCB-containing oil refining waste site in Brandon, Florida (a suburb of Tampa) was evaluated. The evaluation included a determination of toxics in the material being decontaminated as well as all the effluent streams such as ash, air emissions and wastewater. These streams were analyzed for heavy metals, organics, dioxins, furans as well as NO_x, and inorganic acids. Leaching tests were performed on the ash. The results indicated that the PCB was reduced from 5 to 100 ppm to less than 1 ppm in the ash, which was the purpose of the removal action. Although research had indicated that the lead compounds in the ash would become insoluble because they would be complexed with carbon, the ash could not be considered non-leachable based on the EP toxicity tests.

SUMMARY

In 1987, the USEPA started the Superfund Innovative Technology Evaluation (SITE) program to demonstrate new or emerging technology for cleanup of Superfund locations. One of the first technologies planned for testing was the Shirco Infrared System, a furnace which heated a waste on a traveling belt using infrared heaters. The temperature and combustion air levels were sufficient to pyrolyze, crack and then combust the organics present in the waste and convert them to carbon dioxide and water. If products of incomplete combustion (PICs) were formed, they were destroyed in the unit's secondary section (which is a fossil-fuel-fired afterburner).

As the program started, plans were made to characterize a pilot-scale unit. However, the investigation of which locations were available for testing indicated that a full-scale unit having a 100 ton/day capacity was already being used for a cleanup action by EPA's Region IV who asked the SITE program to test it. This full-scale unit was therefore characterized as it was being used and the pilot-scale work was shifted to another location.

The full-scale test described in this paper was at Brandon, Florida (near Tampa) at a former recyle-oil refinery. The material being treated had been placed in a lagoon; it was a thick, black, liquid-appearing waste having 5 to 100 ppm of PCB in it. Although the material appeared to be liquid, it could not be pumped and had to be mixed with the sand or soil surrounding the lagoon before it could be handled by a conveying system. This mixing included neutralization with lime to reduce corrosion of the equipment and the Shirco furnace; the material was sized to less than one-inch diameter before it was introduced to the conveying system and the Shirco unit.

The results and data in this paper are preliminary; however, a full report is being processed and will be issued in about mid-1988. Based on four sets of data, the following results were obtained:

1. The Shirco Infrared System sucessfully achieved the reduction of the PCB content of the feed (3-5 ppm) to less than 1 ppm which was the objective of the removal action.

2. A destruction and removal efficiency for PCB in the gaseous exhaust stream was greater than 99.999 percent (The original PCB content of the lagoon was 5 to 100 ppm).

3. Essentially all of the PCB was destroyed by the burning process, rather than by removal processes, because PCB was not present in the scrubber water.

4. Based on past determinations that any emissions from the stack will be diluted by a factor of 10^{+8}, there were no emissions of any metals or organics which would exceed any existing regulations at ground level. (The air pollution abatement system used for this location, however, was not suitable for the operation. Emissions exceeded the converted grain loading of 0.08 grains/DSCF for two of the four samples taken. The materials of construction for the air pollution abatement system as well as the design of the system should be changed before this particular Shirco unit is used for another study.)

5. The determination of the soluble chromium in the air emissions was not successful. The total amount of chromium, if considered soluble, did not exceed any established or proposed regulations.

6. Lead emissions at ground level were not sufficient to be a significant environmental contaminant.

7. The toxicity characteristic leaching procedure (EP Tox) indicated the material was leachable. These tests will be repeated to assure the results are correct.

8. Metals and organics in the feed, the ash, and the emissions to the atmosphere were determined and will be added to the collective data base. This data base is being used to record information on all hazardous waste systems.

9. More research is necessary to determine how the Shirco unit performs on other hazardous wastes and to get a variation of operating points. A realistic operating cost for a Shirco unit is about $425 per ton of material processed.

BACKGROUND

During the 1950's, an oil refinery, Peak Oil, reclaimed used oil by distilling it at Brandon, Florida (a community near the southeastern edge of Tampa, Florida). The wastes from this processing operation were placed in natural lagoons. These wastes appeared to be a dark thick oil and were found to contain PCBs and lead which were seeping into the ground water. Although the PCBs and lead were known to be contaminants, it was suspected that many other organic materials we now know can be poisonous, toxic or hazardous were also present in the lagoon. The lagoon was located in a sandy soil in a shallow aquifer typical of Florida where the lead and PCBs had started contaminating local drinking water supplies. The Peak Oil site was ranked on the National Priorities List primarily due to the contamination of the local water by PCBs.

EPA Region IV initiated and supervised a removal action at this site. A contract for the removal action work was given to HazTech Inc, an emergency cleanup contractor. HazTech purchased and operated a Shirco Infrared System capable of 100 tons per day operation to perform the cleanup.

PROCESS DESCRIPTION

This Shirco Infrared System was the first full-scale, truck-transportable unit to be used for thermal decontamination of hazardous wastes. The components consisted of a primary unit, secondary unit, an emergency stack, an air pollution abatement system, an exhaust stack and a control van.

The primary unit had a feed distribution system for putting waste onto the woven metal belt which carried the material being treated under the infrared heating rods. The belt travel rate was adjustable. At Peak Oil, the rate of travel was sufficient to keep the feed in the primary section 18 to 19 minutes.

Rotary finger rakes at several locations stirred the material on the belt as it passed under them to assure all the material was exposed to the infrared heat. A blower provided air at selected locations along the belt and could be used to control burning rate of the feed and the location of the feed burning on the belt. The air flow was countercurrent to the feed as it progressed down and off the belt.

As the material (ash) dropped off the belt, it was quenched with water sprays. This quench was scrubber water effluent and was used to reduce the amount of scrubber water effluent for disposal or reprocessing. The ash was screw-conveyed out of the unit into the ash hopper. Then it was removed to a holding area until it was analyzed for PCB content. After it was determined that the PCB content was less than 1 ppm, it was piled in a new location away from the processing area.

The exhaust gases from the primary combustion unit were ducted to the secondary combustion unit. The secondary unit provided about three seconds of retention time at up to 2300°F. It contained bars to increase the turbulence so that any remaining gaseous organics were mixed with air and destroyed. Propane was used as the energy source to supply supplemental heat. Gases from the secondary unit were ducted to the pollution abatement equipment via an induced draft blower located after the scrubber system, prior to the stack.

The air pollution abatement system consisted of a spray quench for the gases followed by a venturi system which had 15-inch minimum pressure drop. During these tests, only one venturi was used. A horizontal packed scrubber system followed the venturi and the water used contained sodium carbonate and sodium hydroxide to neutralize any acid vapors. An emergency stack prior to the pollution abatement system was installed so that if the temperature control system and its interlocks were to fail the air pollution abatement system would not be melted by the hot gases.

The exhaust stack had sample ports and a deck for sampling. A trailer van with the control unit was also part of the installation.

When the unit was fully operational, the feed stream and all effluent streams were evaluated for a 100 ton per day operational point. Over a four-day period, three replicate samples and a duplicate of one of the replicates were taken from the stack gas to be analyzed for PCB, dioxins, furans, semivolatile priority pollutants, volatile organics and heavy metals. Continuous emission monitors were used for O_2, CO_2, CO, THC and NO_x and downwind of the Shirco unit to determine if any air contamination was being created by the operation. Corresponding operating data were collected from the control van while the system was being tested.

Figure 1 shows the sampling locations and the schematic layout of the Shirco Infrared System at Peak Oil.

All samples and analyses were performed at EPA QA level II. This level required an approved sampling and analysis procedure and audits of the procedures. It was a high level of control, but not sufficient for use in a court case.

These tests were conducted for the primary purpose of determining the performance of the Shirco Infrared System. Table 1, shows the properties of the feed material. Although the feed material used during the four days of testing was from the same general pile, it changed the third and fourth day. An estimated 300 tons of feed had been sized and stockpiled for the test, however the estimated 300 tons turned out to be less than 200 tons and a second batch had to be stockpiled. Since the high heating value was about 1640 BTU/lb for the second batch and 2065 BTU/lb for the first batch, the primary unit operated with less air and more infrared heat during the last two days. This also accounts for the wide range of organics and metals shown in Table 1 for the feed material. It appeared that the second batch contained far more inerts (soil and sand) and less of the lagoon contaminants.

RESULTS

PCB

The results of the work indicate the PCB content of the feed was reduced to less than 1 ppm, which was the purpose of the removal action.

Destruction and Removal Efficiency (DRE) for PCB was greater than 99.99 for all tests. Table 2 shows the average of the four samples was 99.99931. Because of the test methods for PCB, it would have taken about three days of sampling for each test to determine if the unit was doing 99.9999 or better. Essentially all of the PCB was destroyed by the burning processes, rather than by removal processes, because PCB was not present in

Reproduced from best available copy.

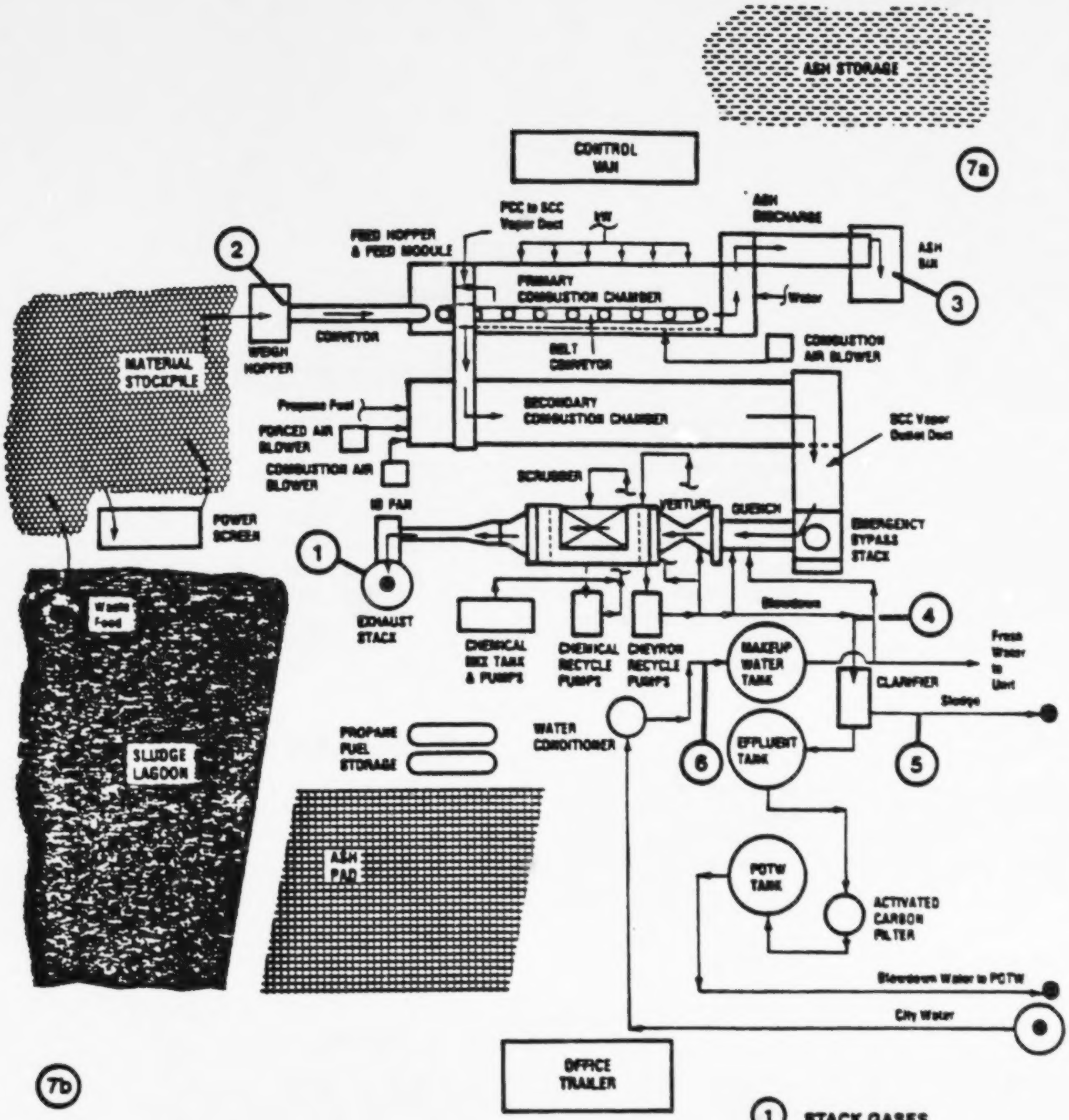

ASH STORAGE
CONTROL VAN
7a
PCC to SCC Vapor Duct
HW
ASH DISCHARGE
ASH BIN
FEED HOPPER & FEED MODULE
2
PRIMARY COMBUSTION CHAMBER
Water
3
MATERIAL STOCKPILE
WEIGH HOPPER
CONVEYOR
BELT CONVEYOR
COMBUSTION AIR BLOWER
Propane Fuel
SECONDARY COMBUSTION CHAMBER
SCC Vapor Outlet Duct
FORCED AIR BLOWER
COMBUSTION AIR BLOWER
SCRUBBER
ID FAN
VENTURI
QUENCH
POWER SCREEN
EMERGENCY BYPASS STACK
1
EXHAUST STACK
Waste Feed
Blowdown
4
CHEMICAL MIX TANK & PUMPS
CHEMICAL RECYCLE PUMPS
CHEVRON RECYCLE PUMPS
MAKEUP WATER TANK
CLARIFIER
Fresh Water to Unit
Sludge
PROPANE FUEL STORAGE
WATER CONDITIONER
6
EFFLUENT TANK
5
SLUDGE LAGOON
ASH PAD
POTW TANK
ACTIVATED CARBON FILTER
Blowdown Water to POTW
City Water
OFFICE TRAILER
7b
1 STACK GASES
2 SOLID WASTE FEED
3 FURNACE ASH
4 SCRUBBER LIQUID EFFLUENT
5 SCRUBBER SOLIDS
6 SCRUBBER WATER INLET
7a AMBIENT AIR (DOWNWIND)
7b AMBIENT AIR (UPWIND)

FIGURE 1

Sampling Locations
Schematic/Layout Diagram
Peak Oil Incineration Unit

Table 1

Waste Feed Solid Analysis

	nanograms per gram
PCB (Total)	3480 to 5850
heptachlorobiphenyl	940 to 2200
hexachlorobiphenyl	1100 to 1700
pentachlorobiphenyl	200 to 490
tetrachlorobiphenyl	400 to 830
trichlorobiphenyl	570 to 820
dichlorobiphenyl	120 to 190
ethyl benzene	40 to 140
methylene chloride	80 to 120
toluene	130 to 300
xylene	260 to 770
	micrograms per gram
antimony	2.1 to 3.6
arsenic	2.0 to 2.9
cadmium	3.9 to 4.6
chromium	20 to 24
copper	44 to 55
strontium	50 to 62
lead	4400 to 5000
vanadium	7 to 11
zinc	950 to 1100
	Percent
moisture	14.2 to 16.6
carbon	7.0 to 7.8
sulfur	1.8 to 2.5
chlorine	less than 0.1
ash	70 to 75
BTU value (HHV)	1640 to 2065 BTU/lb

the scrubber water or ash. A reduction in sample size resulting from an under-capacity cooling system on a sampler limited the ability to obtain greater DRE accuracy.

Particulates

Particulate emissions averaged 0.1015 grains per DSCF, corrected to 7 percent O_2, which was somewhat above the 0.08 regulation set by RCRA. Table 2 indicates the first two samples were above the 0.08 value and the last two samples were less than 0.08 showing the scrubber may not have been suited for the waste being decontaminated at this location. Since the operation was a one-time operation, this does not necessarily indicate that the scrubber system is not suitable for other operations on different materials. The scrubber ducting and stack were of fiberglass construction which was not suitable for this type of operation.

Chlorine

The concentration of chlorine was below the detection limit in the feed and therefore an efficiency of removal (of HCl) could not be determined. The gases were caustic-scrubbed to remove hydrochloric acid and sulfurous acids. Since SO_2 is much harder to remove than HCl, the SO_2 levels in Table 2 are understandably much higher. Table 2 indicates the HCl and SO_2 emission rates in g/hour.

Sulfur

The sulfur in the feed was 300 lbs per hour and the sulfur in the emissions was less than 2.5 lbs per hour. This indicates a removal rate of in excess of 99 percent.

Chromium

Tests for the amount of chromium emitted in the various compounds (soluble and insoluble) were not successful. However, if all the chromium in the feed were emitted through the stack, it would be of such a low concentration that it would not be significant.

Lead

Prior to the test, there was an unconfirmed report that samples of the feed had been roasted and that solubility tests had been run for lead. Results of this bench-scale work indicated that the lead formed an insoluble complex rendering the lead inert. Other bench-scale tests made for lead-containing wastes have indicated that lead remains in the ash and is not emitted.

Table 2

Emission Data

Date of Run	DRE for PCB %	Particulate corrected to 7%O_2, grains/DSCF	HCl g/hr	SO_2 g/hr
8/1/87	99.99967	0.1590	<0.051	27.6
8/2/87	99.9988	0.0939	0.600	1070.0
8/3/87	99.99972			
8/4/87	99.99905	0.0768	0.220	22.0
8/4/87		0.0761	0.200	20.6
Average	99.99931	0.1015	0.2678	285.05

The results of these full-scale emissions tests and the leaching tests on the ash indicated that the bench-scale work did not hold true for the full-scale operation.

Regarding the EP toxicity leach test, Table 3 shows that 31 mg/L of lead are leachable. This compares with a regulatory level of 5.0 mg/L. However, when the Toxicity Characteristic Leaching Procedure (TCLP) test was done for organics, the lead was practically unleachable at 0.011 mg/L (see Table 3). The leach tests will be repeated to check these results. Table 4 shows that the lead had a greater concentration in the ash than the feed, probably because of the volume reduction as the feed was burned.

Cadmium

Cadmium (the elusive metal) was very low in the leach tests (see Table 3). Cadmium analysis of a gas stream often yields poor results based on a material balance. Either the location at which the sample is taken out of the gas stream does not reflect the true cadmium content or the cadmium plates-out in the probe and is not recovered as the sample. Recent research on cadmium seems to indicate that the cadmium plates-out in the probe.

Other Metals

A total of 30 metals were analyzed in the waste feed, ash and stack gas. The results of these analyses are in Table 4.

Semi-volatile Organics

The stack gas was analyzed for over 117 organic compounds and only a small number were detected.

Phthalates were detected, but these were probably from the plastic sample bottles and not the process since they were also detected in the scrubber water streams which also were sampled in plastic bottles. Napthalene was detected at about 1300 ng/m^3 (average) for two out of the four samples taken. Phenol was detected at 500 ng/m^3.

Dioxins and Furans

Dioxins and furans analyses are required whenever PCB is in a waste. In all cases, they indicated less than detectable limits.* All the data from this work will be entered in the research data base presently being assembled.

---

*One test out of four for TCDF indicated a 0.47 microgram/cubic meter recovery (detectable at 0.34 micrograms/liter).

Table 3

Leaching Test Results

	EP Toxicity		TCLP Analysis	
Parameter	Average mg/L	Regulatory Level, mg/L	Average Level, mg/L	Regulatory Level
Arsenic	0.020	5.0	.007	5.0
Barium	1.35	100	.25	100
Cadmiun	.099	1.0	.008	1.0
Chromium	.037	5.0	.037	5.0
Lead	31	5.0	.011	5.0
Mercury	.0015	0.2	ND*	0.2
Selenium	ND*	1.0	.031	1.0
Silver	.031	5.0	.059	5.0
Only TCLP compounds detected are listed below				
Acrylonitrile	-	-	.013	5.0
Methylene chloride		-	.020	8.8
Toluene			.0020	14.4
1,1,1, Trichloroethane			.0006	30
Trichloroethane			.0006	.07

---

*Not detected

Table 4

Metals Analysis

	micrograms/gram, ug/g		
Parameter	Solid Waste Feed	Ash	Stack gas
Aluminum	1625	2500	<210
Antimony	2.15	3.3	91
Arsenic	2.55	2.6	38
Barium	505	757	675
Beryllium	.168	.3	.11
Boron	NA	NA	625
Cadmium	4.15	4.1	1920
Calcium	37500	50000	1680
Chromium	22	27	270
Cobalt	.75	2	<11
Copper	49	64	420
Iron	2050	2600	440
Lead	4800	6400	58000
Lithium	ND	ND	21
Magnesium	850	1050	180
Manganese	47	55	12
Mercury	ND	ND	<.10
Molybdenum	ND	ND	50
Nickel	8	10	42
Phosphorus	790	770	0
Selenium	ND	ND	3.2
Silicon	NA	NA	780
Silver	2.0	4.0	10
Sodium	5550	5600	18600
Strontium	57	76	10
Sulfur	20500	24000	160000
Thalluim	ND	ND	630
Titanium	41	115	<50
Vanadium	9	13	<25
Zinc	1030	1060	9400

ND - Not determined
NA - Not analyzed
The stack gas contained 0.1015 grains/DSCF of particulate (One grain = 64.8 mg)

Since this test collected data for one operating point for one material, more research should be done on the Shirco system to collect data for more operating conditions on different feed materials. To do this, we have performed a SITE test using the Shirco Infrared pilot plant system at the Rose Township, Michigan waste location.

Cost and Economics

An economic analysis concluded that the cost of using a Shirco unit could be as low as $200 per ton of contaminated material or as high as $800 per ton depending on the equipment usage factor considered realistic for the project to be evaluated. A projected realistic average cost per ton of contaminated material is $425 per ton.

DEMONSTRATION OF THE PYRETRON™ ENHANCED OXYGEN BURNER AT THE U.S. EPA COMBUSTION RESEARCH FACILITY

by

Grigory Gitman, Mark Zwecker and Tom Wechsler
American Combustion, Inc.
Norcross, Georgia,

Larry Waterland and Johannes Lee
Acurex Corporation
Mountain View, California

and

Robert E. Mournighan and Laurel J. Staley
U.S. Environmental Protection Agency
Cincinnati, Ohio 45268

ABSTRACT

The Pyretron™ developed by American Combustion Inc. is an enhanced oxygen burner designed to be retrofitted to an existing incinerator. As part of the Superfund Innovative Technology Evaluation (SITE) program, a Pyretron was installed on the rotary kiln system at the U.S. EPA's Combustion Research Facility (CRF) where it was used to treat a mixture of soil and decanter tank tar sludge from coking operations, listed waste K087. This paper presents a preliminary evaluation of the Pyretron's performance during this test.

Introduction

The Superfund Amendments and Reauthorization Act (SARA) of 1986 established the Superfund Innovative Technology Evaluation (SITE) Program to promote the development and use of innovative technologies to treat Superfund and hazardous wastes. As part of the SITE program, the Pyretron™ Thermal Destruction System, developed by American Combustion, Inc., was demonstrated at the U.S. EPA Combustion Research Facility (CRF) in Jefferson, Arkansas.

The purpose of the demonstration was to evaluate three claims made by American Combustion which represent improvements in hazardous waste incinerator burner design. These claims are as follows:

1. That the Pyretron, with its oxygen enhancement and proprietary process control system, reduces transient particulate emissions that occur when solid material is intermittently fed to a rotary kiln.

2. That the improved heat transfer and process control provided by the Pyretron make it possible to achieve significantly higher waste throughput rates.

3. That the cost savings resulting from the higher throughput rates offset the cost of the required oxygen resulting in an economical process.

Although the demonstration was completed early this year, all of the data have not been thoroughly evaluated yet and, as a result, the final report on this project will not be available until later this year. This paper will report on the data available at this time. After a more detailed description of the Pyretron and how it was installed at the CRF, a more detailed description will be given of the results obtained thus far.

Description of the Pyretron and of the CRF's Rotary Kiln

Figure 1 is a schematic diagram of the Pyretron enhanced oxygen burner. The Pyretron combustion system utilized for this demonstration had a total rated firing capacity for the kiln and afterburner of 3.5MM BTUs/hr. The burners had turndown ratios which exceeded 10/1 and were designed to operate at excess oxygen levels up to 600%. For this test the Pyretron is designed to burn propane and not liquid hazardous waste. The Pyretron burner technology uses a parallel-staged combustion approach based on the independent introduction of either oxygen or air into the burner combustion chamber. Oxygen flowing through the center of the burner partially oxidizes and thermally pyrolyzes the propane mixing concentrically around it resulting in, among other things, the formation of radiant soot microparticles. Radiant heat transfer from these microparticles is the main mechanism for energy transfer for the combustion of the solid material being treated in the rotary kiln. Although this also happens with conventional burners, the higher temperature of soot microparticles inside the flame envelope resulting from oxygen enhancement intensifies this effect. These soot microparticles are further burned out by contact with the oxygen and air streams flowing concentrically around the pyrolytic flame zone.

The Pyretron Thermal Destruction System installed at the CRF included two enhanced oxygen burners like the one described above, accompanying gas trains and a process control system which dynamically controls the air/oxygen/fuel ratios based on readings of CO, O_2 and pressure in the rotary kiln and afterburner.

This computerized process controller for dynamic incineration process control is able to maintain process temperature and excess oxygen levels and to respond to rapid process deviations by dynamically changing the relative amounts of combustion air and oxygen fed to the incinerator. These changes are based on measurements of CO, O_2, and pressure between the kiln and afterburners. By varying the air-to-oxygen ratio, the amount of nitrogen fed to the incinerator is closely controlled. Nitrogen occupies a major fraction of a conventional incineration combustion chamber volume

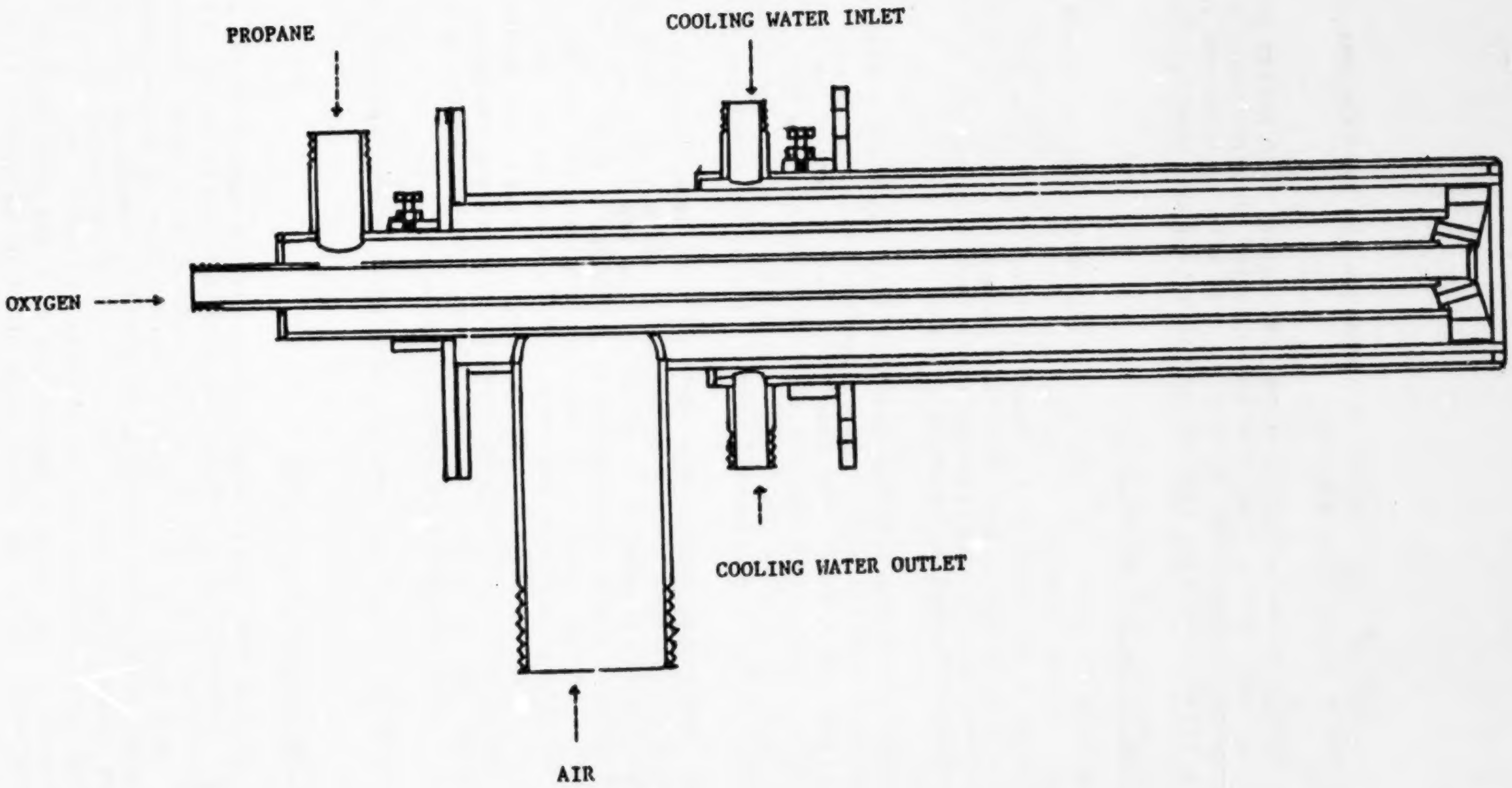

PROPANE
COOLING WATER INLET
OXYGEN
COOLING WATER OUTLET
AIR

Figure 1. Schematic of the Pyretron

and is a major heat sink. Figure 2 shows how the Pyretron was incorporated into the CRF's rotary kiln system.

The design characteristics of the CRF rotary kiln system are provided in Table 1. For testing, the kiln was operated at approximately 1800°F and the afterburner was operated at 2050°F. The kiln rotation was such as to provide a solids residence time of approximately one hour (.2 rpm).

Description of Demonstration Tests

As mentioned previously, the objective of the demonstration tests was to evaluate the performance of the Pyretron Thermal Destruction System in comparison to a conventional air based incineration system utilizing the CRF rotary kiln system (RKS). For this comparison, the only modification to the CRF RKS was the substitution of the conventional air burner system by the Pyretron Thermal Destruction System.

A waste stream was selected for this test which was a mixture of waste material from the Stringfellow Superfund site and decanter tank tar sludge, listed waste K087. The resulting waste stream which is characterized in Table 2 has a heat content of approximately 8600 BTUs/lb. The POHCs designated for this waste are several hazardous polynuclear aromatic hydrocarbons (i.e., the principal organic hazardous constituents).

Eight tests were conducted as part of this demonstration. There are two reasons why so many tests were required. First, the claims made about the Pyretron were comparative in nature and so required that tests be conducted without oxygen enhancement to establish a basis for later comparisons. Second, it was necessary to determine the maximum feed rate for both air and oxygen enhanced operation in order to evaluate one of the claims. This required two separate tests. First, the maximum amount fed per charge must be determined. Second the maximum frequency at which those charges can be fed must be determined. Table 3 lists the tests conducted as part of this SITE demonstration.

For each test, all feed and effluent streams were sampled using standard methods.

Test Results/Conventional System

The optimum feed charge mass and the optimum mass feedrate attainable utilizing a conventional air-based incineration system on the CRF rotary kiln consisted of a mass charge of 21 pounds at a charging interval of 12 minutes. This level was determined after a series of optimization trials and was based on emission levels as measured by continuous emission monitors, combustion chamber temperatures and the ability to control process upsets. Higher feed rates destabilized the process too much. This is shown by test data from a trial run using a mass charge size and charging interval that were an increment above the levels determined to be optimum (i.e., at

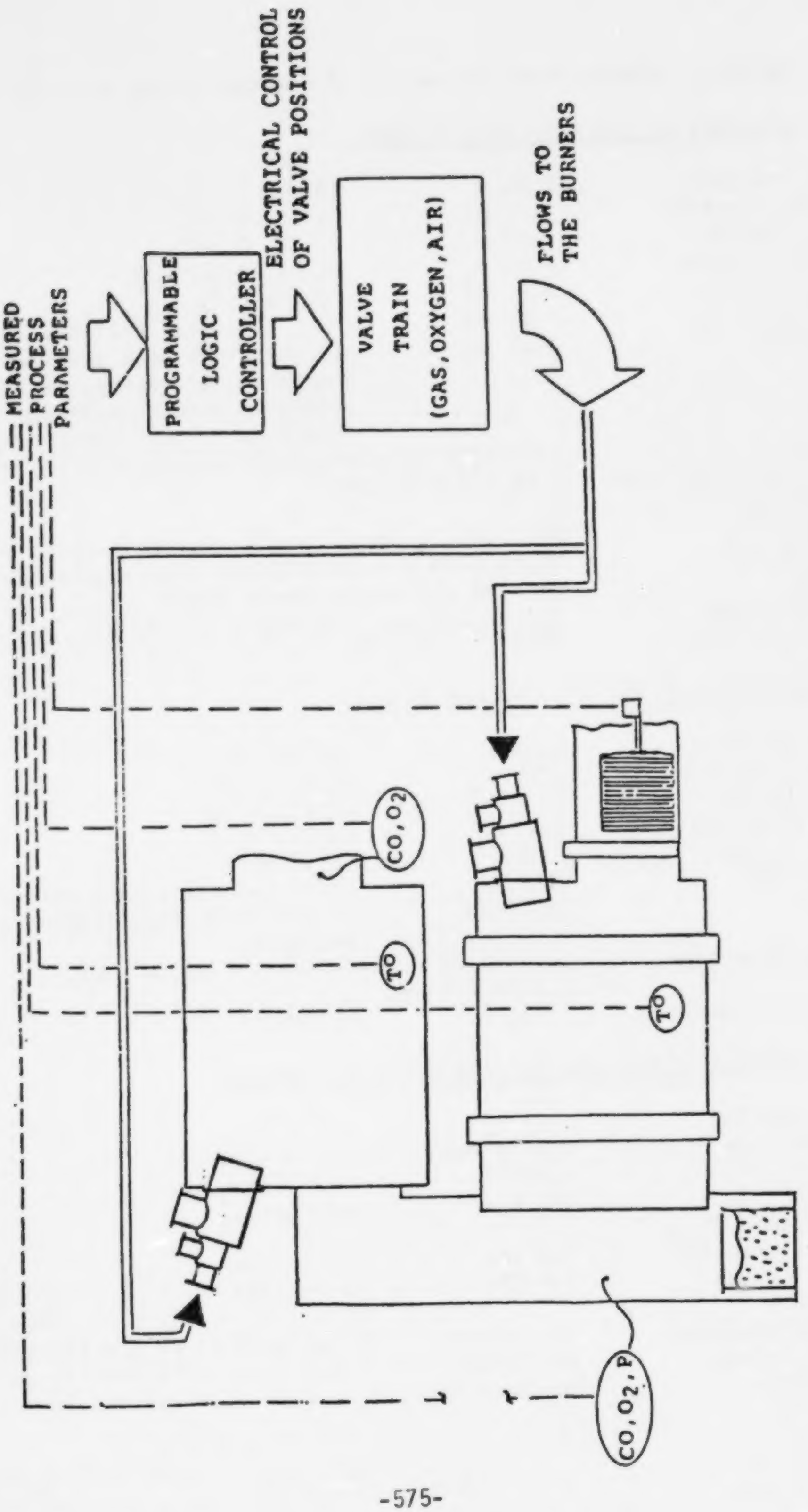

MEASURED
PROCESS
PARAMETERS
PROGRAMMABLE
LOGIC
CONTROLLER
ELECTRICAL CONTROL
OF VALVE POSITIONS
VALVE
TRAIN
(GAS,OXYGEN,AIR)
FLOWS TO
THE BURNERS
CO,O$_2$
T°
T°
CO,O$_2$,P

Figure 2. Pyretron Thermal Destruction System Process Diagram

TABLE 1. Design Characteristics of the CRF Rotary Kiln System

Characteristics of the Kiln Main Chamber

Length, outside	2.61 m	(8 ft, 7 in)
Diameter, outside	1.22 m	(4 ft, 0 in)
Length, inside	2.13 m	(7 ft, 0 in)
Diameter, inside	0.95 m	(3 ft, 1-1/2 in)
Chamber volume	1.74 m^3	(61.36 ft^3)
Construction	0.63 cm	(0.25 in) cold rolled steel
Refractory	12.7 cm	(5 in) thick high alumina castable refractory, variable depth to produce a frustroconical effect for moving solids
Rotation	Clockwise or counterclockwise 0.2 to 1.5 rpm	
Solids retention time	1 hr (at 0.2 rpm)	
Feed system		
Liquids	Pos. displacement pump via water-cooled lance	
Semiliquids	Moyno pump via front face, water-cooled lance	
Solids	Metered twin-auger screw feeder	
Containerized	5.7 L (1.5 gal) fiberpack ram feeder	
Temperature (max)	1000°C (1850°F)	

Characteristics of the Afterburner Chamber

Length, outside	3.05 m	(10 ft, 0 in)
Diameter, outside	1.22 m	(4 ft, 0 in)
Length, inside	2.74 m	(9 ft, 0 in)
Diameter, inside	0.91 m	(3 ft, 0 in)
Chamber volume	1.80 m^3	(63.6 ft^3)
Construction	0.63cm	(0.25 in) thick cold rolled steel
Refractory	15.24 cm	(6 in) thick high alumina castable refractory
Gas residence time	Depends on temperature and excess air, 1.2 to 2.5 sec	
Temperature (max)	1,200°C	(2,200°F)

Characteristics of the Air Pollution Control System

System capacity		
Inlet gas flow	1.07 m^3/min	(3,773 acfm) at
	1,200°C	(2,200°F)
	101 kPa	(14.7 psia)
Pressure drop		
Venturi scrubber	7.5 kPa	(30 in. wc)
Packed column	1.0 kPa	(4 in. wc)
Liquid Flow		
Venturi scrubber	77.2 L/min	(20.4 gpm) at 69 kPa (10 psig)
Packed column	116 L/min.	(30.6 gpm) at 69 kPa (10 psig)
pH control	Feedback control by NaOH solution addition	

TABLE 2. Waste Characterization [a,b]
Parts Per Million

Naphthalene	49772
Acenaphthalene	11722
Fluorene	6397
Phenanthrene	22569
Anthracene	6764
Fluoranthene	11529
Pyrene	11036
2-Methylnaphthalene	3457
Dibenzofuran	3926
Miscellaneous PNA	5017
Miscellaneous Unknowns	1031

[a] 60% by weight K087
40% Stringfellow Soil

[b] Average over 9 composite samples

TABLE 3. Summary of 8-Week Pyretron Demonstration Program Test Conditions

Test/Purpose						-Afterburner-	
	Charge size, lbs	Charge entered, min.	Feed Rate, lb/hr	Kiln T, °F	Kiln O_2, %	Temp., °F	O_2,
1 Same as test 2 except using air-only burner	8	4	120	1870	8.9	2017	11.2
2 Test burn Stringfellow waste with 4500 ppm C_2Cl_6 and 4500 ppm $C_6H_3Cl_3$ with oxygen enhancement (per Region IX request)	8	4	120	1866	13.7	2017	13.0
3 Determine max feed rate with air-only burner	21	12	105	1906	11.3	2036	7.7
3A Duplicate of test 3	21	12	105	1781	11.8	2030	7.4
4 Assess oxygen-enhanced operation at feed rate determined in tests 3 and 3A	21	12	105	1772	17.1	2022	15.2
5 Assess oxygen-enhanced performance at max feed mass/charge at feed rate determined in test 3	34	19.5	105	1778	14.5	2042	14.6
6 Determine maximum mass/charge with oxygen enhancement	21	6	210	1794	14.8	2010	13.5
6A Duplicate test 6	21	6	210	1814	15.4	2017	15.5

24 lbs/10 minutes). These data are provided in Figure 3. In this case, emissions or "puffs" were high enough to impede operation of the kiln. Depletion of oxygen in the kiln resulted in flame outs and in excessively high CO levels exiting the kiln and CO breakthroughs from the afterburner. This depletion of oxygen typically occurred immediately following batch charges as waste combustion consumed all the available oxygen.

When attempts were made to increase air flows to provide the additional oxygen required, residence times were reduced below levels necessary for complete combustion and CO levels were therefore increased. Several flameouts also occurred at that time. In addition, gaseous emissions were observed on several occasions due to the loss of negative pressures in the kiln.

With the high BTU waste stream selected for this demonstration, the kiln was unable to dissipate the heat build-up at the maximum mass charge size and feed interval selected for this test. This build-up is partly a function of the limited capability of the conventional air-based flame to be turned down to reduce auxiliary fuel input while maintaining sufficient flows of oxidizer into the kiln as well as auxiliary flame stability to conduct proper incineration.

Data from stripchart recordings of the series of tests at the optimum mass charge and optimum feedrate for air-only operation are provided in Figure 4. As can be seen from these graphs, oxygen content and temperature levels in the kiln were maintained within the operating limitations of the kiln. Carbon monoxide levels at the kiln exit reached moderate levels, however, these levels were within the capacity of the afterburner system so that stack emissions stayed within regulatory requirements.

Test Results/Pyretron Thermal Destruction System

Figure 5 presents the data from testing the Pyretron Thermal Destruction System. The mass charge size was maintained at the 21 pounds utilized with the conventional air-based incineration system, however, the charge interval was reduced from 12 minutes to 6 minutes. This reduction in the charge interval represents a doubling in the throughput rate with the Pyretron system as compared to the conventional incineration system.

As can be seen from the graphs, the Pyretron system provided temperature control in both the kiln and afterburner. Oxygen levels at the kiln exit were maintained at sufficiently high levels and CO at the kiln exit was at a minimum with no indication of CO at the stack.

This data depicts the ability of the the oxygen enhanced Pyretron to process waste at a faster rate than air-only combustion. Dynamic water injection was used to control temperature in the kiln in the oxygen-enhanced mode.

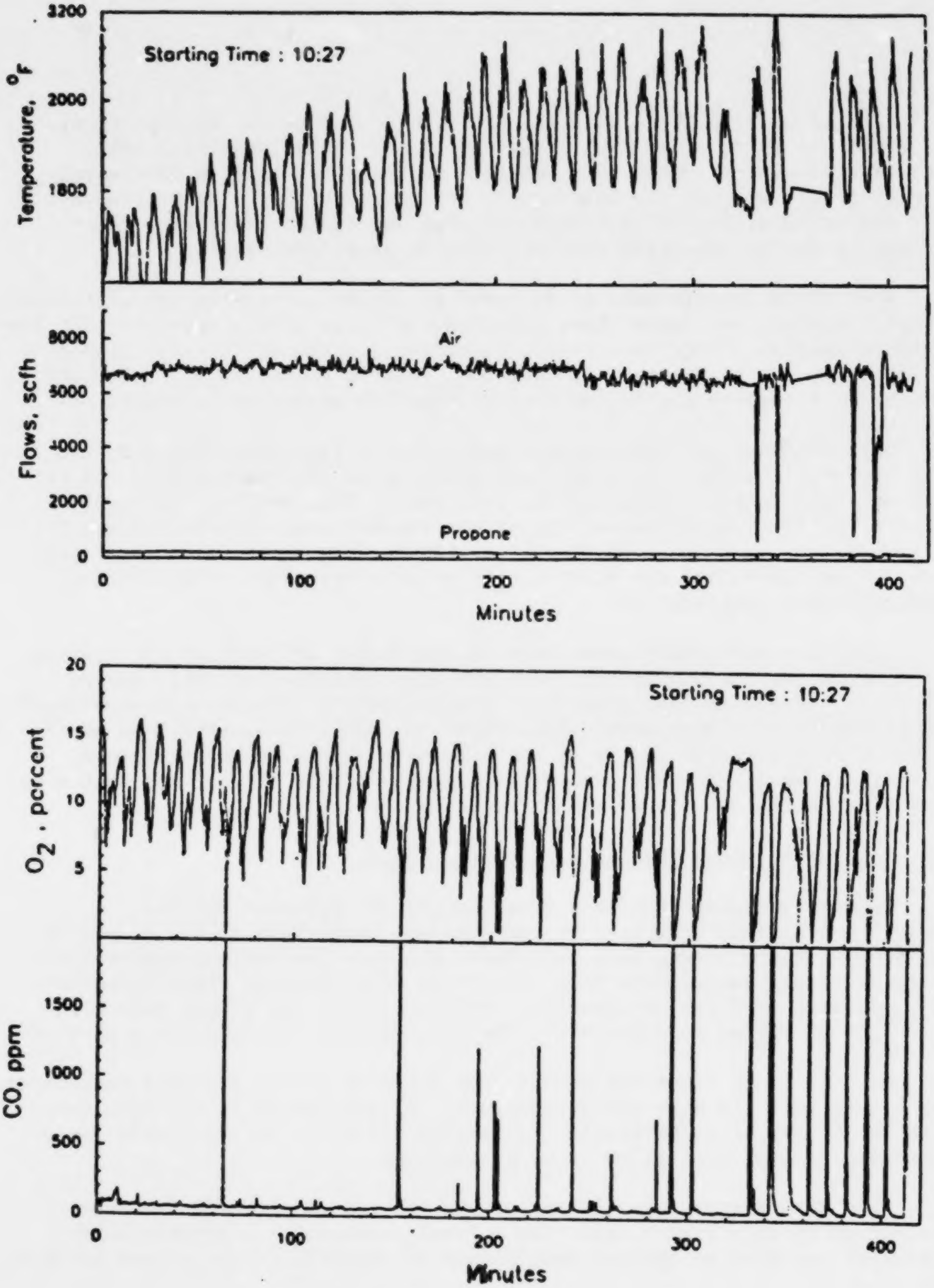
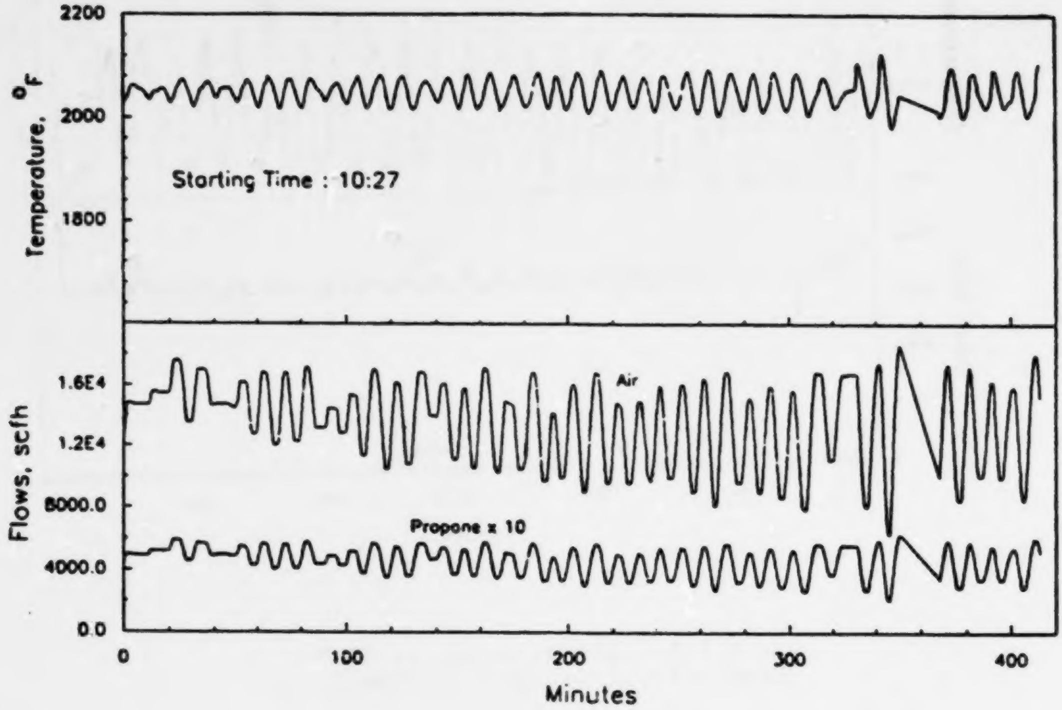


Figure 3. C.R.F. Kiln Data for 12-08-87 Conventional System - 24 lbs/10 min.

Figure 3. (Cont.)

C.R.F. Afterburner Data for 12-08-87
Conventional System - 24 lbs/10 min.



C.R.F. Stack Data for 12-08-87
Conventional System - 24 lbs/10 min.

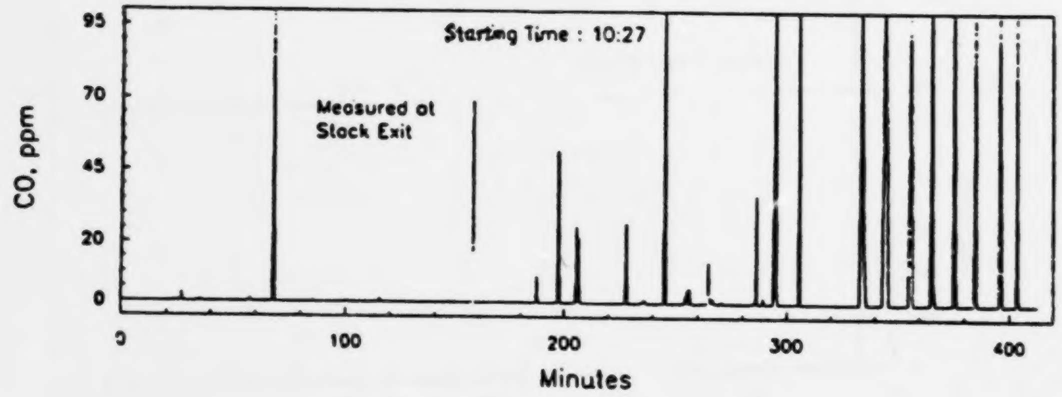
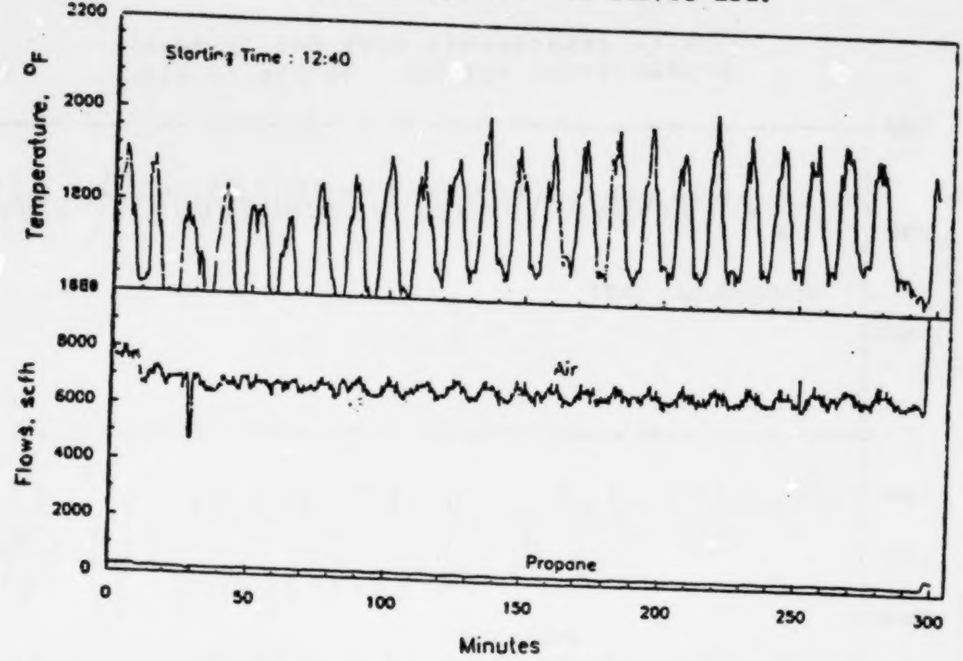


Figure 4.

C.R.F. Kiln Data for 12-09-87
Conventional System - 21 lbs/12 min.



C.R.F. Kiln Data for 12-09-87
Conventional System - 21 lbs/12 min.

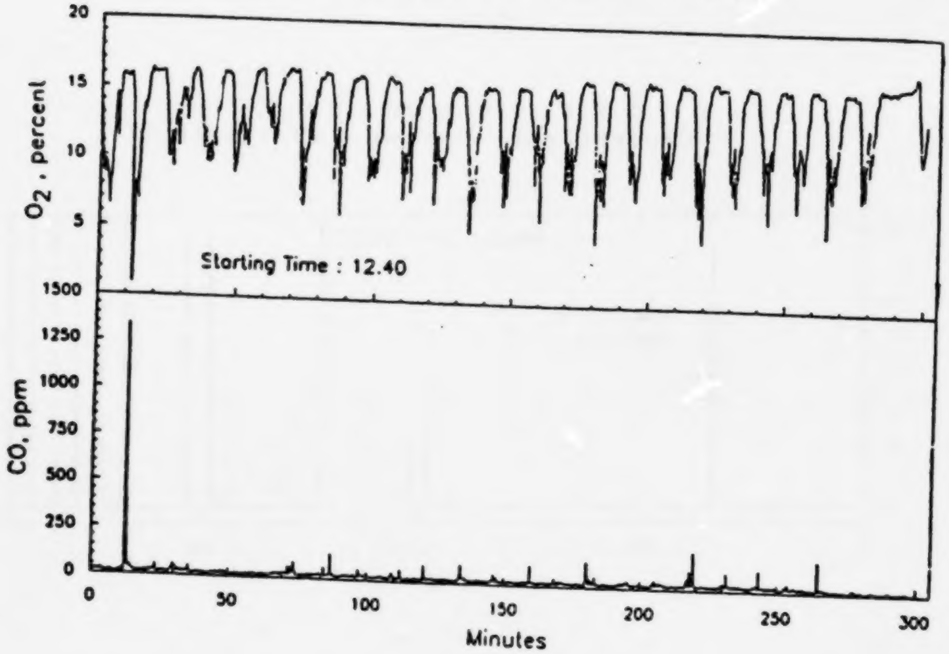
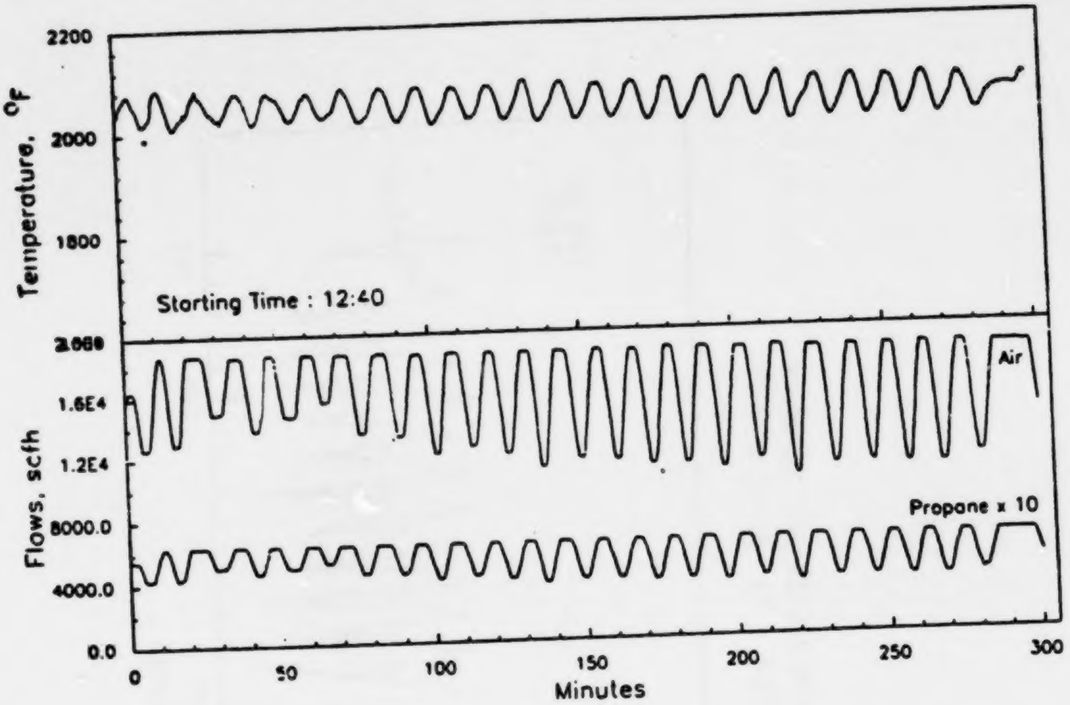


Figure 4. (Cont.)

C.R.F. Afterburner Data for 12-09-87
Conventional System - 21 lbs/12 min.



C.R.F. Stack Data for 12-09-87
Conventional System - 21 lbs/12 min.

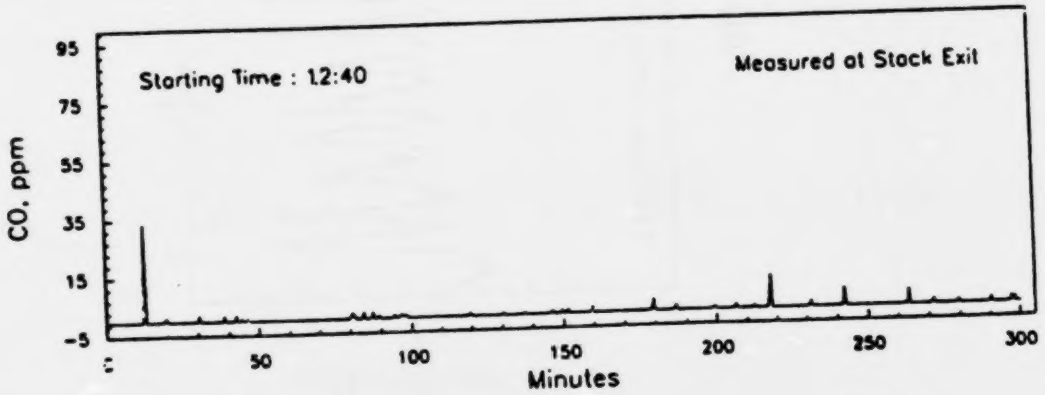


Figure 4. (Cont.)

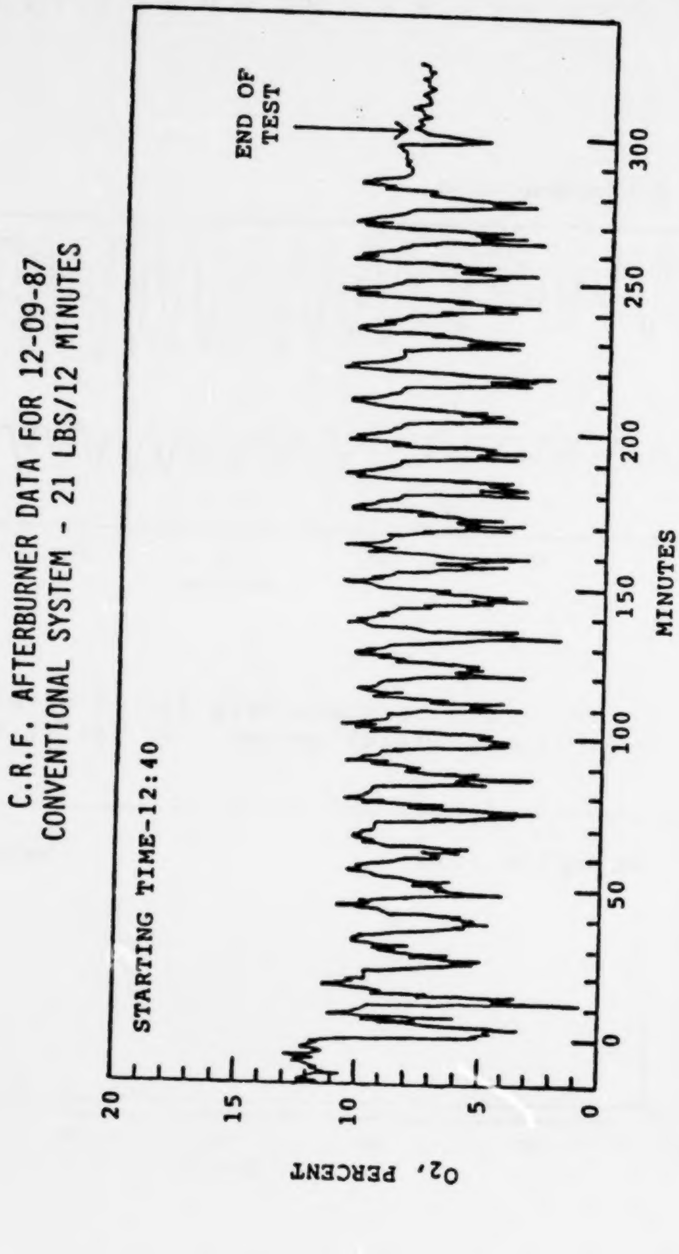


Figure 5.

C.R.F. Kiln Data for 1-21-88
Pyretron System - 21 lbs/6 min.

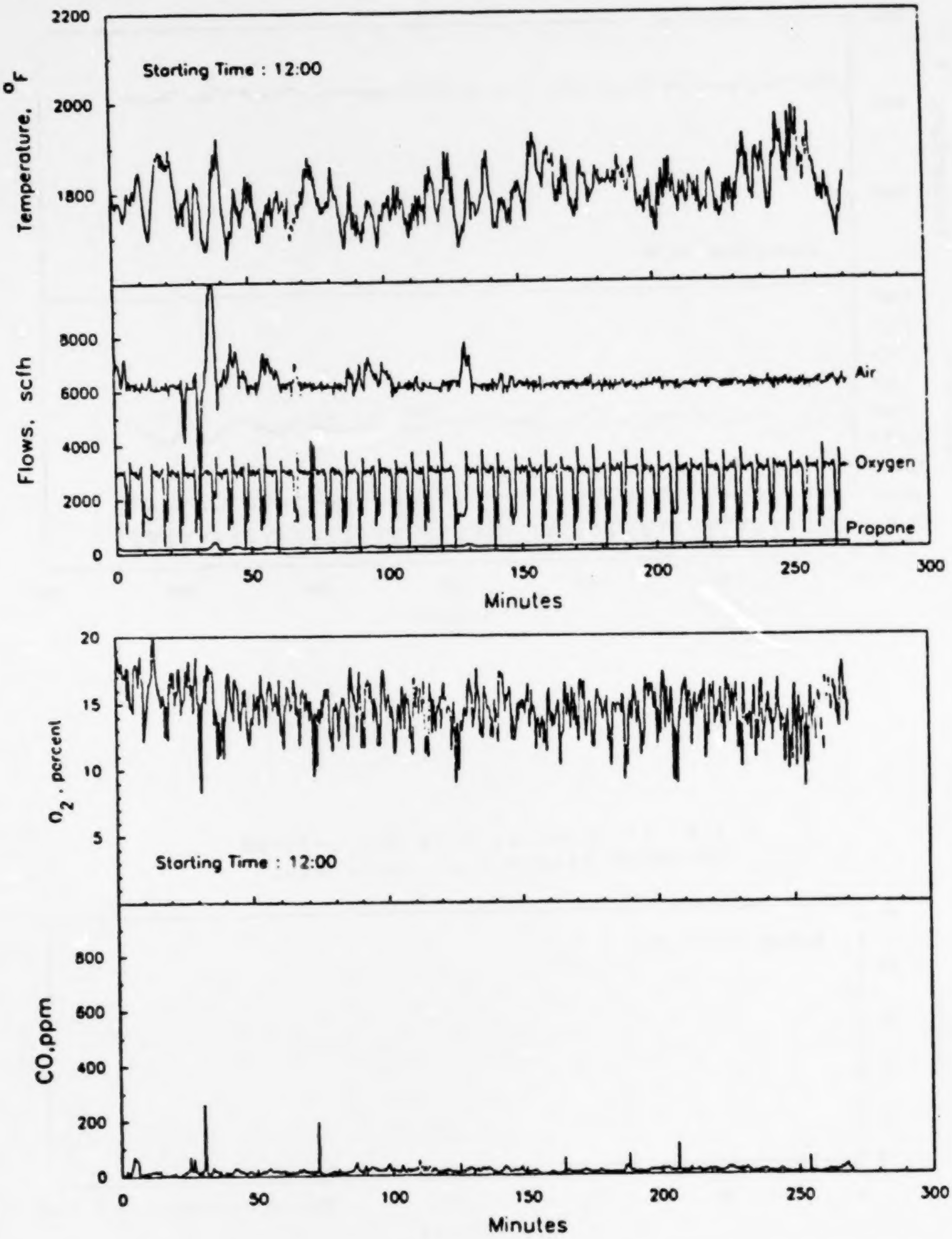
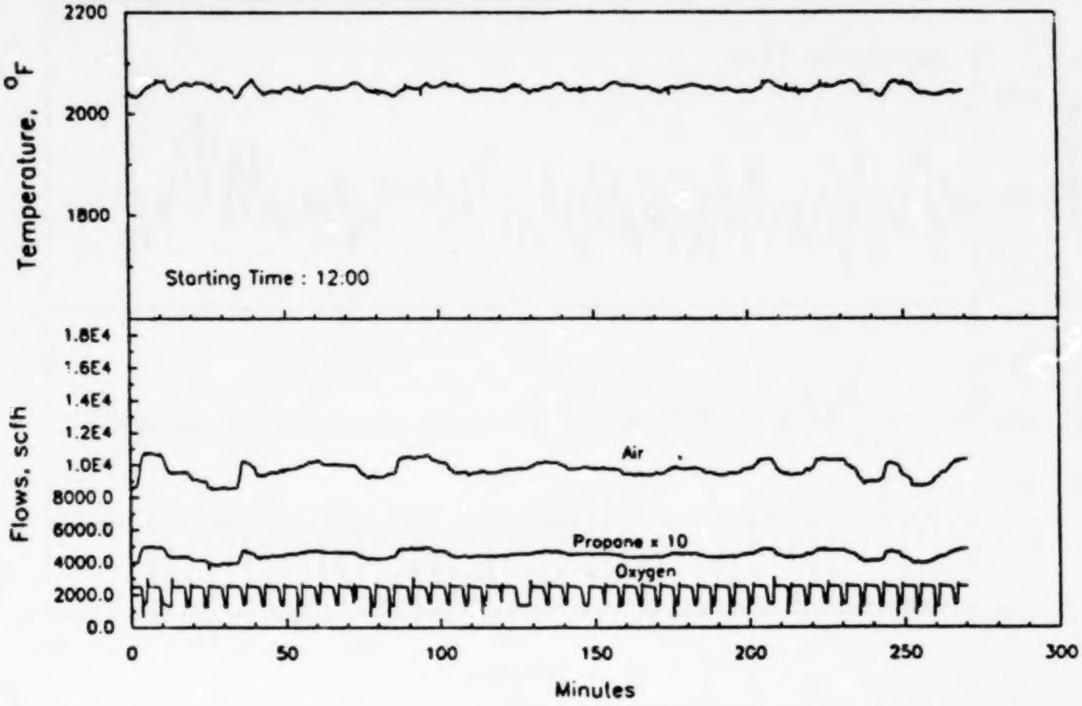
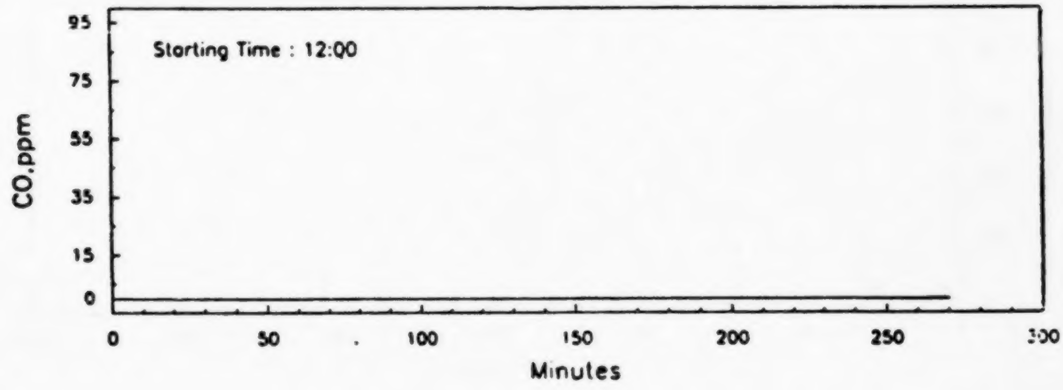


Figure 5. (Cont.)

C.R.F. Afterburner Data for 1-21-88
Pyretron System - 21.lbs/6 min.



C.R.F. Afterburner Data for 1-21-88
Pyretron System - 21 lbs/6 min.



A final set of data is provided in Figure 6 representing an attempt to challenge the Pyretron Thermal Destruction System by increasing the size of the batch charge by 60%. For this test the mass of the batch charge was increased to 34 pounds in an attempt to determine the capability of the system to handle the so-called "puffs" which are experienced with many incinerators immediately following a batch charge. As can be seen from the data, even with a 60% increased batch charge size, the system was able to maintain sufficient oxygen concentration in the kiln and CO levels at the kiln exit well within the capacities of the afterburner system. Again, during this test using the Pyretron Thermal Destruction System, there was no CO emitted from the afterburner.

Destruction and Removal Efficiencies and Particulate Emission

Destruction and Removal Efficiencies (DRE) exceeded 99.9999% for all tests. No POHCs were detected in the stack gas.

These results show that, even with increased throughput rates, 99.99% DRE is still achievable.

Particulate emissions for each of the 8 tests are summarized in Table 4. Data are corrected to 7% O_2 only for the air-only tests. At this point, the best way to make this correction in cases where oxygen enhancement is used has not been determined.

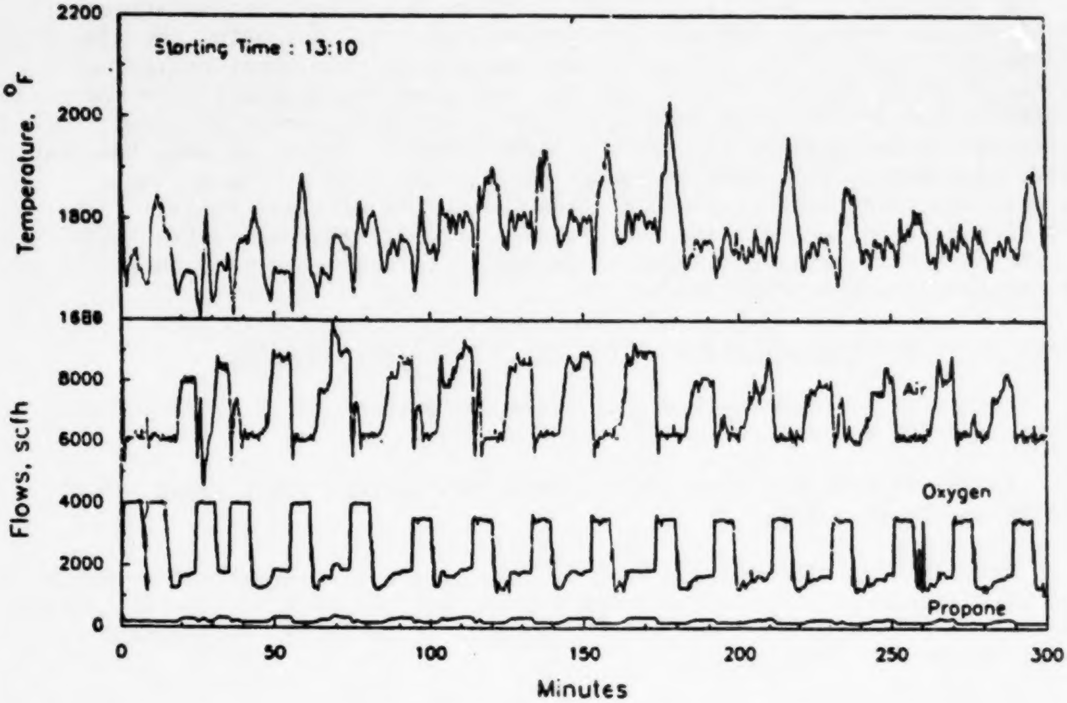
Conclusions

Although all of the data is not in yet, the data available so far supports two of the claims made about the Pyretron. That is, for the waste tested and the conditions under which it was tested, transient emissions, i.e., "puffs", were reduced, and waste feed rates could be increased while still meeting 99.99% DRE.

Final evaluation of the claims made about the Pyretron's performance will have to await final analysis of all the data. This data evaluation should be completed by October, 1988.

Figure 6.

C.R.F. Kiln Data for 1-14-88
Pyretron System - 34 lbs/19.5 min.



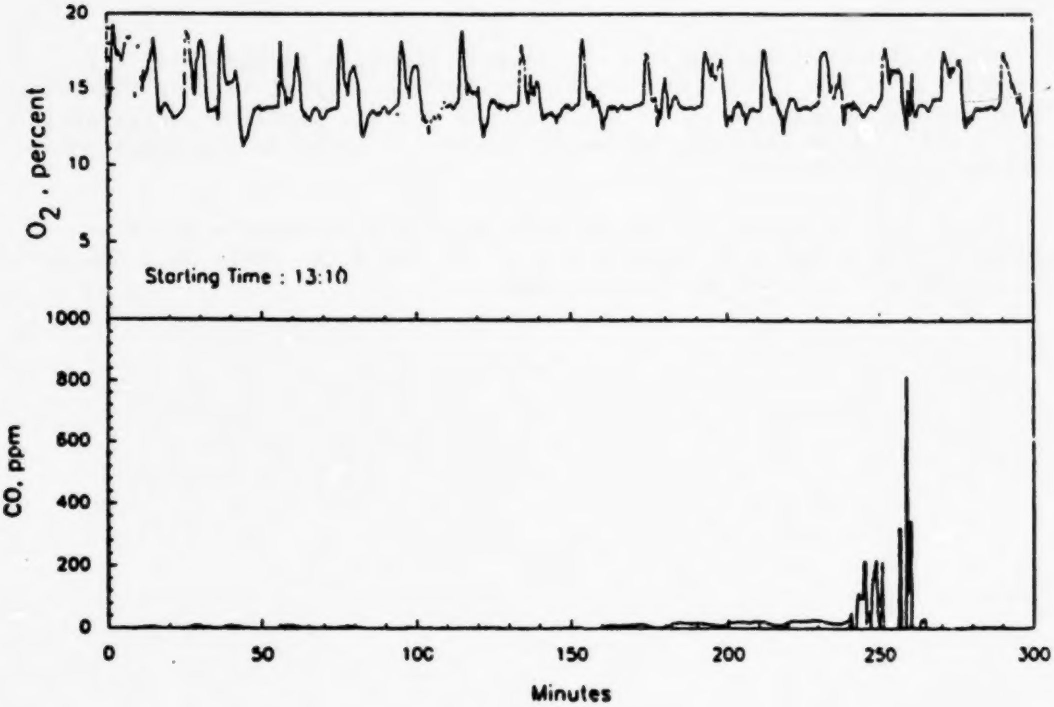
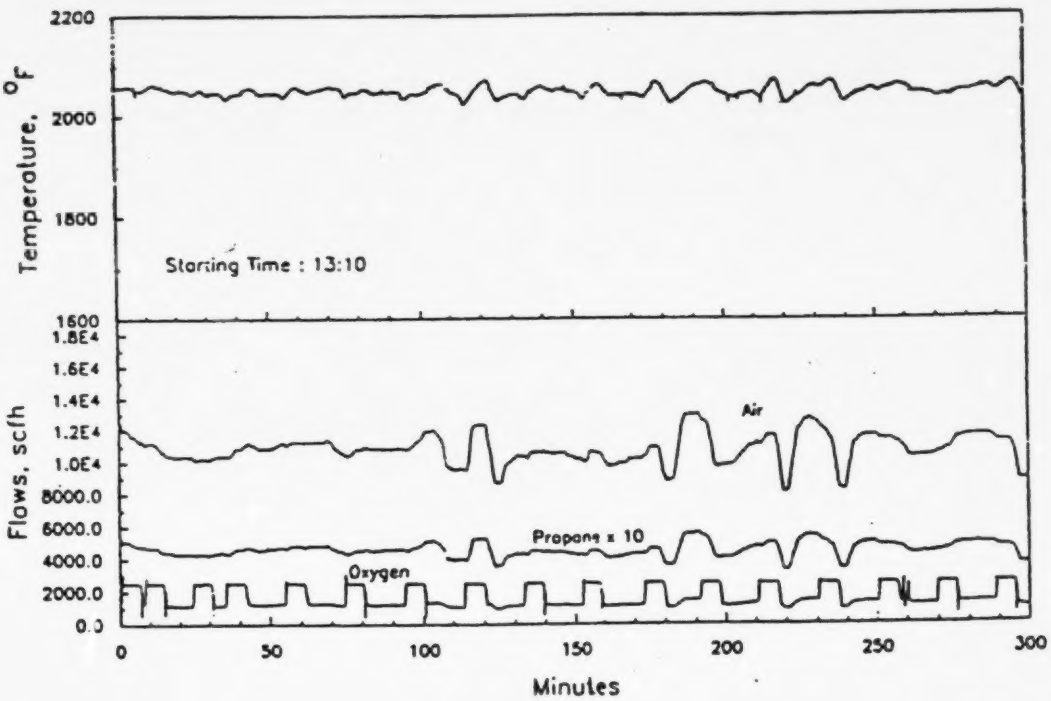


Figure 6. (Cont.)



C.R.F. Afterburner Data for 1-14-88
Pyretron System - 34 lbs/19.5 min.

TABLE 4. Particulate Emissions Data

Test	Particulate[a] Concentration mg/dscm	Particulate Concentration[b] mg/dscm	Particulate Concentration (uncorrected) gr/dscf
1	8.0	8	.0016
2	9.0	9	.0018
3	99.0	47	.0124
4	59.0	29	.0082
5	63.0	28	.0106
6	21.0	10	.0032
7	37.0	28	.0073
8	38.0	39	.0086

[a] Corrected to 7% O_2 for the air-only tests

[b] Corrected to 7% O_2 considering the effect of oxygen enhancement

TERRA VAC IN SITU VACUUM EXTRACTION PROCESS SITE DEMONSTRATION

Peter A. Michaels
Enviresponse, Inc.
Edison, NJ 08837

Mary K. Stinson
U.S. Environmental Protection Agency
Hazardous Waste Engineering Research Laboratory
Releases Control Branch
Edison, NJ 08837

ABSTRACT

Field demonstration testing of the Terra Vac In Situ Vacuum Extraction process has been conducted in Groveland, Massachusetts under the auspices of the Superfund Innovative Technology Evaluation (SITE) program. This site has been contaminated mainly by trichloroethylene, which was used as a degreasing solvent by the machine shop that is still in operation at the site.

Vacuum extraction works by air stripping organics-contaminated soil. A vacuum pump draws contaminated air from a well through a separation device and into activated carbon canisters. Effectiveness is determined primarily by posttest measurements of volatile organic concentrations.

Among the factors to be considered in technology selection and implementation for site remediation are site characteristics, site preparation, equipment size requirements, health and safety precautions, and waste products collection and disposal. Site conditions may have a significant impact on a demonstration. Operation in the winter months in a cold climate under severe weather conditions may involve higher risks and costs.

INTRODUCTION

This SITE program demonstration was planned to demonstrate the effectiveness of vacuum extraction technology in removing contamination to a depth of 25 feet. The Terra Vac In Situ Vacuum Extraction demonstration, the process for which a U.S. patent has been issued, was conducted on the property of an operating machine shop in Groveland, Massachusetts. The property is at the southwest corner and the highest elevation of the Groveland Wells Superfund site, which contains the municipal water supply system for the town of Groveland. The Superfund site has three sources of contamination, one of them being the Valley Manufactured Products Co., Inc. machine shop. A leaking storage tank and former improper storage and handling practices of waste oils and degreasing solvents have caused the subsurface soil contamination with volatile organic compounds, mainly trichloroethylene.

As is the case with many field projects, modifications had to be made to the original demonstration plan to accommodate the situations encountered in the field involving drilling, sampling, equipment installation, and operation during the worst months of a severe New England winter. The results obtained from this project will be applied by EPA to predict success of the vacuum extraction technology at other Superfund sites.

SITE CONTAMINATION AND CHARACTERISTICS

The vadose zone at the location of the vacuum extraction wells is approximately twenty-five feet in depth and is divided into two segments by a clay lens that is three to four feet thick. Contamination is present above and below the clay lens. Contaminated water is present as perched water on this clay lens and as groundwater, which flows in a northwesterly direction into a body of water known as Mill Pond.

The contamination is present mainly as trichloroethylene (TCE); trans-1,2-dichloroethylene; 1,1,1-trichloroethane; and chloroform. The only one of the contaminants that was actually in use as a degreasing solvent at the machine shop was trichloroethylene. The other compounds are thought to be biodegradation products of TCE. Trichloroethylene is by far the contaminant present in the greatest amount. During the pretest soil sampling, the highest concentration detected in the soil was 1600 ppm of TCE, approximately 18 to 20 feet below the surface at the southeasternmost portion of the Valley site.

SITE PREPARATION AND LOGISTICS

The site was prepared prior to mobilization of equipment in order to conduct the test in an orderly and economical manner. Minor cleaning and grubbing was required to assure access to the extraction wells and monitoring well area. Of most importance in the field preparations were

- Procurement, placement, and outfitting of the two field trailers required at the job site

- Providing the utilities required, mainly electric power

- Providing for personnel and equipment decontamination areas

The trailers at the site were located in the northern end of the parking lot on the opposite side of the building from the test area. One trailer was for EPA and Terra Vac personnel, while the other trailer housed the sampling and analytical (S&A) contractor's equipment and personnel. Both trailers were supplied with 120V/60Hz electricity and furnished with telephones, desks, and chairs. The S&A trailer had a basic equipment list that consisted of

- oven, refrigerator, hood
- two gas chromatographs (GCs) with associated integrators and columns. One GC had a flame ionization detector (FID) and the other an electron capture detector (ECD).
- organic Vapor Analyzer (OVA)
- personal computer with printer
- gas cylinders for nitrogen, argon/methane mixture, hydrogen, and compressed air
- electronic balance
- gas tight syringes - 50 ml, 5 ml, and 1 ml
- liquid syringes - 100 µl, 50 µl, 10 µl, and 5 µl
- glass bulbs, Tedlar bags
- barometer, thermometers, and manometer
- solvents - methanol, hexane
- miscellaneous equipment including garden sprayer, brushes, buckets, tool chest, notebooks, and assorted health and safety equipment

The EPA trailer was equipped with the following:

- portable OVA with FID
- portable photoionizer
- portable GC with photoionization detector (PID) and computer
- calibration gases
- sound level meter
- various health and safety gear including respirator facepieces with combination cartridges, SCBAs, hardhats, rubber gloves, rubber boots, Tyvek suits and boots, ear plugs, first aid kit, and stretcher

- portable rotameter, vacuum gauges

- two-way radios

- water cooler and coffee maker

The 120V/60Hz power supply was tapped off the street utility pole and metered to the two trailers. The 480V/3-phase/60Hz power requirement was tapped off an existing 480V line in the Valley plant This line was run inside the building through a circuit breaker and meter for the purpose of supplying power to the vacuum pump skid.

Two decontamination areas were provided at the site: one for personnel and one for equipment. The equipment decontamination area was used primarily for drill rig augers. Steam cleaning was employed to cut down on the amount of water collected in the tarpaulin-lined bermed area. Decon water collected was pumped into 55-gallon drums and temporarily stored on site to await final disposal. Water for the steam generator or "jenny" came from a hose connection on the Valley building.

EQUIPMENT LAYOUT AND SPECIFICATIONS

The equipment layout is shown in Figure 1, and specifications are given in Table 1 for the equipment used in the initial phase of the demonstration. This equipment was later modified when unforeseen circumstances required a shutdown of the system. The vapor-liquid separator, activated carbon canisters, and vacuum pump skid were inside the building, with the stack discharge outside the building. The equipment was in an area of the machine shop where used cutting oils and metal shavings had been stored.

Four extraction wells and four monitoring wells (MW1 - MW4) were drilled south of the shop. Each well was installed in two sections, one section to just above the clay lens and one section to just below the clay lens. The extraction wells were screened above the clay and below the clay. As shown in Figure 2, the well section below the clay lens was isolated from the section above by a bentonite portland cement grout seal. Each section operated independently of the other. The wells were arranged in a triangular configuration, with three wells on the base of the triangle (VE2, VE3, VE4) and one well at the apex (VE1). The three wells on the base were called barrier wells. Their purpose was to intercept contamination, from underneath the building and to the side of the demonstration area, before this contamination reached the main extraction well (VE1). It was the area enclosed by the four extraction wells that defined the area to be cleaned.

INSTALLATION OF EQUIPMENT

Well drilling and equipment setup were begun on December 1, 1987. A mobile drill rig was brought in, equipped with hollow-stem augers, split spoons, and Shelby tubes. The locations of the extraction wells and monitoring wells had been staked out previously based on contaminant concentration profiles from a previously conducted remedial investigation and from bar punch probe soil gas monitoring.

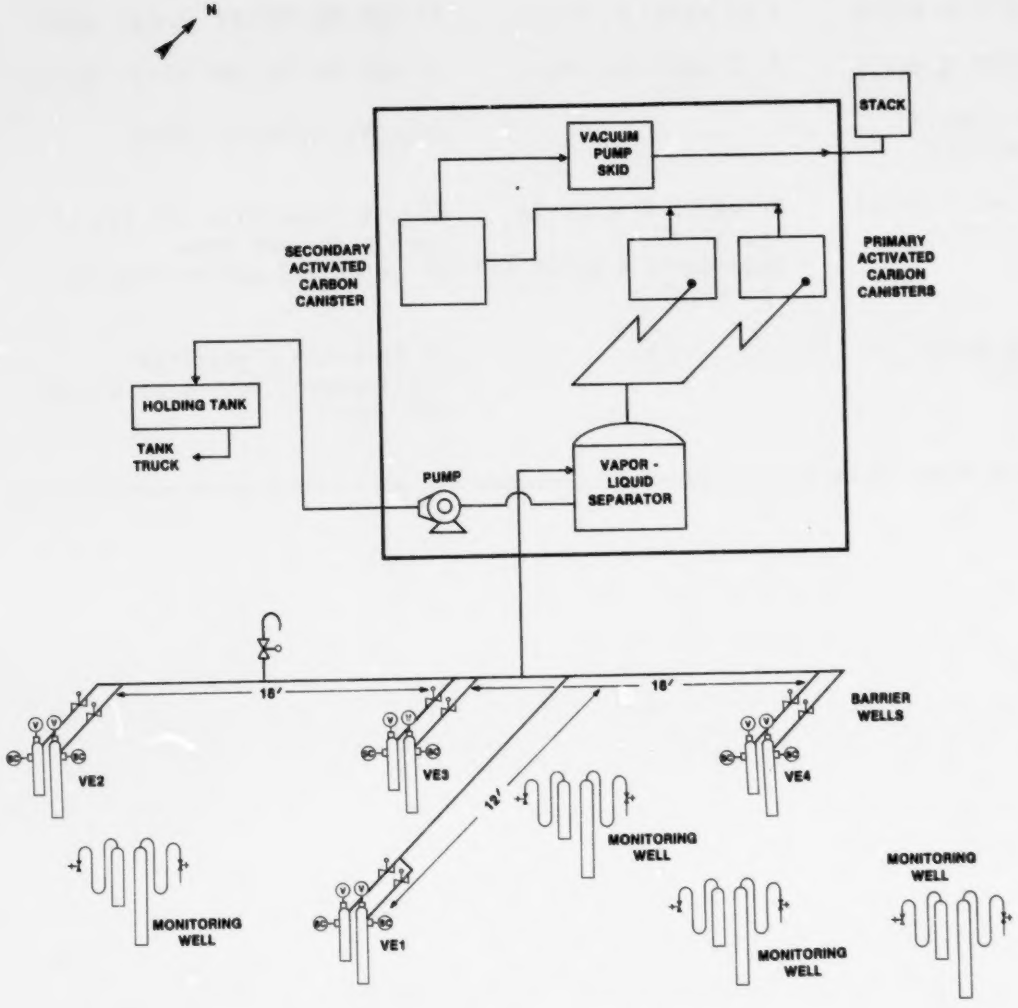

N
STACK
VACUUM PUMP SKID
SECONDARY ACTIVATED CARBON CANISTER
PRIMARY ACTIVATED CARBON CANISTERS
HOLDING TANK
TANK TRUCK
PUMP
VAPOR - LIQUID SEPARATOR
18′
18′
BARRIER WELLS
VE2
VE3
VE4
12′
MONITORING WELL
MONITORING WELL
VE1
MONITORING WELL
MONITORING WELL

Figure 1. Schematic diagram of equipment layout at Terra Vac SITE Program demonstration site, Groveland, Mass.

TABLE 1. EQUIPMENT LIST

Equipment	Number required	Description
Extraction wells	4 (2 sections each)	2" SCH 40 PVC 24' total depth
Monitoring wells	4 (2 sections each)	2" SCH 40 PVC 24' total depth
Vapor-liquid separator	1	192-gal capacity, steel
Activated carbon canisters	Primary: 4 units in parallel Secondary: 4 units in parallel	55-gal drums with 200 lbs of carbon in each drum 2" inlet and outlet nozzles
Vacuum pump skid	1	25 HP motor - positive displacement lobe type blower - 3250 rpm

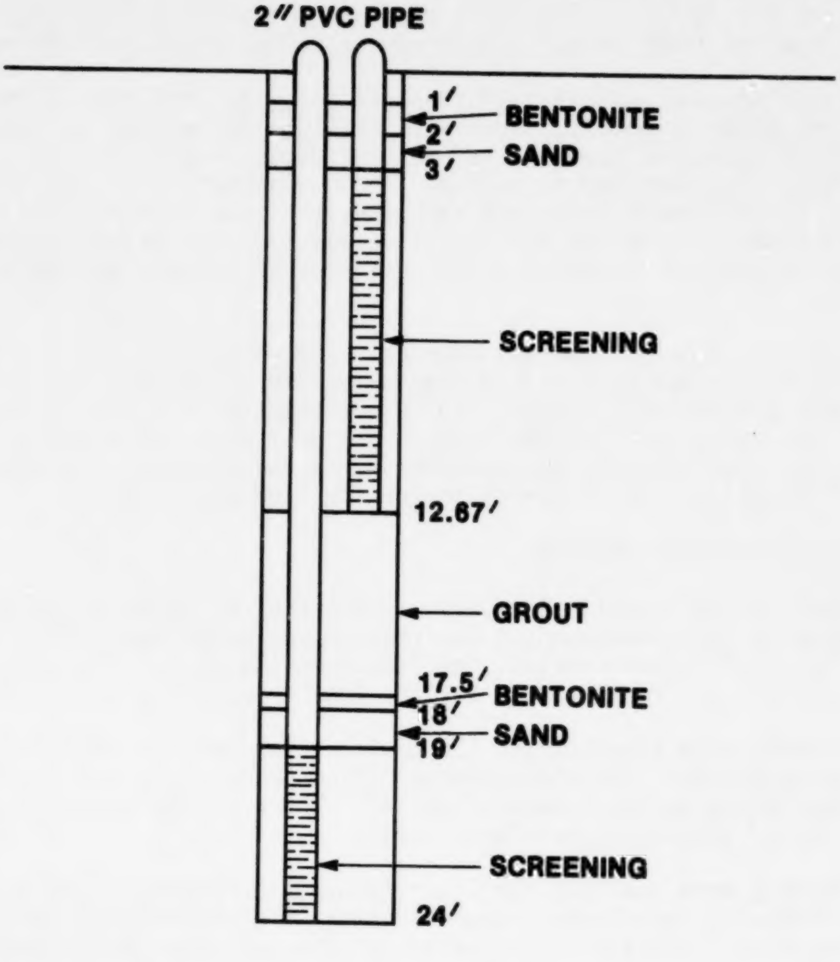

2″ PVC PIPE
1′
BENTONITE
2′
SAND
3′
SCREENING
12.67′
GROUT
17.5′
BENTONITE
18′
SAND
19′
SCREENING
24′

Figure 2. Schematic diagram of an extraction well.

Each well drilled was sampled at 2-foot intervals with a split spoon pounded into the subsurface by the drill rig in advance of the hollow stem auger. The hollow stem auger would then clear out the soil down to the depth of the split spoon, and the cycle would continue in that manner to a depth of 24 feet. The drilling tailings were shoveled into 55-gallon drums for eventual disposal. After the holes were sampled, the wells were installed using 2-inch PVC pipes screened at various depths depending upon the characteristics of the soil in the particular hole. The deep well was installed first, screened from the bottom to various depths. A layer of sand followed by a layer of bentonite and finally a thick layer of grout were required to seal off the section below the clay lens from the section above the clay lens. The grout was allowed to set overnight before the shallow well pipe was installed at the top of the grout. A layer of sand bentonite and grout finished the installation.

While sampling and well installation was going on, the rest of the equipment was being assembled. Four-inch flexible PVC piping was installed to a distribution header at the inlet of the activated carbon canisters. Two-inch flexible PVC piping was used to each of the four primary activated carbon canisters. The 2-inch outlets from each canister were piped with flexible PVC to a 4-inch header. A 4-inch flexible line was then run to the vacuum pump skid, which discharged through a silencer to the atmosphere through a 4-inch line.

When the well installation was complete, the three wells in line were connected to each other by a 4-inch line or header. Each well section was equipped with a block ball valve. The main extraction well was connected to the 4-inch header by a 4-inch PVC line. Each well head had a septum from which to take gas syringe samples, a connection for a vacuum gauge, and coupling connections to attach a portable rotameter for flow measurement.

SAMPLING AND ANALYTICAL PROGRAM

The sampling and analytical program is the tool by which to judge the effectiveness of this technology. The program was conducted in five separate periods: the pretreatment period, the commissioning period, the active treatment period, the midtreatment period, and the posttreatment period.

Soil borings were taken during the pretreatment, midtreatment, and posttreatment periods. The midtreatment period occurred 28 days after the start of the 56-day active treatment period. The posttreatment period started after the end of the active treatment period.

Soil borings were analyzed for volatile organic compounds (VOCs) using headspace screening techniques, purge and trap GC/MS techniques, and the EP-TCLP procedure. Additional properties of the soil were determined by sampling using a Shelby tube, which was pressed hydraulically by the drill rig into the soil to a depth of 24 feet. These Shelby tube samples were analyzed to determine physical characteristics of the subsurface stratigraphy, such as moisture, bulk density, porosity, pH, and grain size. (See Table 2.) These parameters, which may influence the bulk transport of volatile organics through the subsoil, will be used to define the basic soil characteristics.

TABLE 2. ANALYTICAL METHODS

Parameter	Analytical method	Matrix
Grain size	ASTM D422-63	Soil borings
pH	SW846* 9040	Soil borings
Moisture (110°C)	ASTM D2216-80	Soil borings
Particle density	ASTM D698-78	Soil borings
Oil and grease	SW846* 9071	Soil borings
EP-TCLP	F.R. 11/7/86, Vol. 51, No. 216, SW846* 8240	Soil borings
TOC	SW846* 9060	Soil borings
Headspace VOC	SW846* 3810	Soil borings
VOC	GC/ECD	Soil gas
VOC	GC/ECD	Process gas
VOC	SW846* 8010	Separator liquid
VOC	SW846* 8010	Groundwater
VOC	Modified P&CAM 127	Activated carbon
VOC	SW846* 8240	Soil borings

*Third Edition, November 1986.

The active treatment period was redesigned to be a total of 56 days in order to be able to project a cleanup time for the site with greater confidence than was possible in the original 14-day period. During the active treatment period, gas sampling was conducted according to the schedule in Table 3.

Active treatment analyses were done in the field in the mobile laboratory. Gas samples were collected by syringes, and for concentrations above 5 ppm a GC with an FID detector was used. For low concentrations a GC with an ECD detector was used. Computer-generated curves show TCE concentration versus time for each well, both shallow and deep. This enabled close tracking of the progress of the vacuum extraction process.

Other measurements were taken routinely during the course of the active treatment period, including

- flowrates from each well section, with a portable rotameter
- vacuum at each well section
- moisture content of well-head gas, using Modified Method 4 sampling train
- temperature
- Wattmeter readings on vacuum pump skid

Activated carbon samples were taken from all spent carbon canisters to check for VOC loading. This was done both as a check on the calculations for the quantity of VOC extracted from the soil and to gather data on adsorption at various inlet concentrations of VOCs.

During this project, blanks, splits, and duplicates were collected as required to assess the accuracy and precision of the sampling and analytical methods employed for all critical parameters.

STARTUP AND OPERATING EXPERIENCE

The initial startup and operation of the system proceeded according to plan. Startup commenced on December 16, 1987 with high extraction rates of TCE and perched water from the clay lens. After less than a week's operation it was decided to break for the holiday season. Upon arriving back at the job site, the piping, valves, and fittings were found to be frozen.

The entire piping network was then electrically traced and insulated, and the system was started up during the week of January 11, 1988. Large quantities of water were being extracted with rates up to 600 gallons per day. Activated carbon was being used up at the rate of four canisters or 800 pounds per day. The system was shutdown on January 15 in order to scale up the equipment. This was necessitated by the much higher than expected recovery rates of volatiles and water. After the new equipment was installed, the system was restarted on February 10.

The new equipment consisted of

TABLE 3. ACTIVE TREATMENT SAMPLING SCHEDULE

Sample locations	Week 1	Weeks 2 & 3	Weeks 4 & 5	Weeks 6, 7, & 8
VE1-S VE1-D	Twice per day	Once per day	Every other day	Every third day
VE2-S,D VE3-S,D VE4-S,D	Once per day	Every other day	Every other day	Every third day
MW1-S,D MW2-S,D MW3-S,D MW4-S,D	Once per day	Every other day	Every other day	Every third day
Separator outlet	Every other day	Once per week	Once per week	Once per week
Primary carbon outlet	Every other day	Every day	Every day	Every other day
Secondary carbon outlet	Every other day	Once per week	Once per week	Once per week

- 1000-pound capacity stainless steel carbon canisters, 45" diameter x 64" height
- 1000-gallon capacity vapor-liquid separator
- 1-HP centrifugal pump to pump liquid from the separator
- 2000-gallon holding tank for contaminated water

The new activated carbon canisters were topped off with an additional 200 pounds each of carbon from unused 55-gallon drums. The system was then piped up with two primary carbon canisters in parallel followed by a single secondary unit.

The small centrifugal pump was installed to take suction from the drain on the 1000-gallon vapor-liquid separator. A level switch activated the pump when the level in the separator rose to the half-full mark. The pump would then pump a 300-gallon batch of contaminated water approximately 80 feet to the holding tank, shutting off automatically when activated by the low-level switch.

The new carbon canisters had operating times that made operation of the unit much easier. The first set of primary canisters lasted five days; the second set, nine days; and the third set, fourteen days. At this point the program had reached the midpoint of the demonstration test.

After a five-day break, including a weekend, during which time midtreatment soil sampling was done by split spoons adjacent to the installed monitoring wells, the unit was restarted and run for an additional 28-day period.

WASTE DISPOSAL

As mentioned before, decontamination water during drilling and sampling operations was collected and pumped into 55-gallon drums. Contaminated groundwater collected by the vacuum pump system was initially pumped into 55-gallon drums. These drums froze and had to be stored on site until they were thawed with the advent of warmer weather. When the equipment change was implemented, most of the water collected was stored in the 2000-gallon capacity holding tank.

A tank truck came periodically to the site to pump the water from the holding tank. This contaminated water was manifested and sent to a biological treatment facility that was fully permitted and in regulatory compliance. The 55-gallon drums of spent carbon along with the drilling tailings were overpacked in salvage drums, manifested, and shipped as flammable solids to a permitted incineration facility. The thawed drums of contaminated water eventually were pumped into the tank truck for biological treatment. The frozen drums had bulged and so were not suitable to be recycled. They were air dried and cut up as scrap metal.

POSTSCRIPT

The major objectives of the demonstration have been to determine the ability of the technology to reach an acceptably low level of contaminant concentration in the soil; to assess the effectiveness in various soil types; to gather capital and operating costs; and to gain performance and reliability information. In addition an attempt will be made to establish a correlation between volatile organic constituent (VOC) concentrations in soils and concentrations in extracted vapors.

Extensive sampling and analytical work will continue to be performed and operating parameters monitored in order to evaluate the vacuum extraction process in such a way as to bear up under close scientific scrutiny and predict the likely success of this technology at other Superfund sites.

ACKNOWLEDGMENTS

The authors wish to thank Mr. James R. Ciriello of the U.S. Environmental Protection Agency Region I, Boston, Massachusetts for his unstinting efforts during the course of this project. A special note of gratitude is to be given to Mr. Thomas Quinlan of the Valley Manufactured Products Co. Inc. for his special support and cooperation that helped make this project a successful one.

WHITE ROT FUNGUS DEVELOPMENT PROGRAM

by: John A. Glaser
U. S. Environmental Protection Agency
Cincinnati, Ohio 45268

ABSTRACT

The development of the white rot fungus *Phanerochaete chrysosporium* as a degrader of hazardous waste shows some promising opportunities for the development of new hazardous waste treatment technologies. The fungus secretes a mixture of strongly oxidizing enzymes that are identified as a major component in the ability of this microorganism to degrade xenobiotics. A line of research that strives to uncover the activity relationships of the components of this enzyme mixture is only one component of the EPA's overall development scheme for this organism. The enzyme studies re designed to determine optimal enzyme compositions necessary for the degradation of targeted pollutants. The control technology development is devoted to the degradation of organic wastes associated with the remediation of wood preservation technology sites. A soil treatment technology based on the fungus is currently being developed and evaluated at the bench scale. Testing this soil technology at field scale may be possible in the next calendar year. An associated water treatment is further advanced to pilot scale testing.

THE IMPACT OF A MODEL ORGANIC LEACHATE ON SLURRY WALL PERFORMANCE

Richard M. McCandless and Andrew Bodocsi, Ph.D.
Department of Civil & Environmental Engineering
University of Cincinnati
Cincinnati, Ohio 45221

ABSTRACT

Soil-bentonite slurry cutoff walls are frequently constructed to control the migration of contaminated groundwater at Superfund sites. Previous research by these authors and others has focused on the hydraulic characteristics of slurry walls and the potential for the development and/or in situ remediation of hydraulic defects (windows). Nearly all of this work, however, has involved the use of a clean model groundwater and uncontaminated slurry wall construction materials. Moreover, although numerous authors have studied the effects of various chemicals on the hydraulic performance of soil-bentonite backfill, most of these studies have involved the use of permeant liquids having high contaminant concentrations and the testing of small (laboratory size) backfill samples. The purpose of this study is to assess the impact of a more representative model organic leachate on the long-term performance of a near pilot-scale model slurry wall. Data and conclusions cannot be presented at this time.

A model organic leachate has been designed for this project based upon a statistical formulation developed by SAIC, Inc. and published in an EPA report entitled "Composition of Leachates From Actual Hazardous Waste Sites". Primary criteria for the design of a three-component model leachate included maximum possible representativeness in terms of level of occurrence in the statistical formulation, miscibility and stability in aqueous solution, compatibility and lack of synergistic effects, and manageable health and safety requirements. With these factors in mind, a model organic leachate containing phenol, acetone and N,N-dimethylacetamide at a total net organic fraction of 6.0% by volume is proposed for use.

The slurry wall test tank used by the authors in the conduct of previous studies has been substantially modified for this project. A circular test wall approximately 508 mm (20 inches) in diameter, 559 mm (22 inches) in height and 102 mm (4 inches) thick will be surrounded by a partitioned granular leachate collection zone which, in turn, will be surrounded by a second cutoff wall serving to contain the leachate within the leachate collection

zone. Vertical standpipes will be used to periodically sample leachate which has permeated through the test wall at each of three different elevations. The leachate samples will then be analyzed for each of the three organic components and the results will be used along with measured flow parameters to generate chemical and hydraulic breakthrough curves for the model. Testing is scheduled to commence in the spring of 1988 and may continue for a time period of up to one year, depending upon the aggressiveness of the model organic leachate.

BIOLOGICAL TREATMENT OF AQUEOUS ORGANIC HAZARDOUS WASTE

by: Lisa M. Brown
U.S. Environmental Protection Agency
Cincinnati, Ohio 45268

Margaret K. Koczwara and Richard J. Lesiecki
Department of Civil and Environmental Engineering
University of Cincinnati
Cincinnati, Ohio 45221-49TE

ABSTRACT

As part of a program to perform hazardous waste treatment technology assessments, the USEPA has been directed to evaluate technologies applicable to the treatment of organic wastes. Biological treatment is one of several technologies being evaluated for treatment of hazardous waste at the USEPA Test & Evaluation Facility.

While biological treatment is a potential technology for aqueous organic waste containing contaminants in concentrations up to 10,000 ppm, these contaminants may be present in the waste at concentrations toxic to the microorganisms, or they may be recalcitrant and require a different treatment approach. Also, some compounds are more readily degraded in aerobic systems, while others may require an anaerobic system for degradation.

At the USEPA Test & Evaluation Facility, bench-scale studies are being conducted to determine toxicity/biodegradability of hazardous waste constituents in both aerobic and anaerobic systems. Pilot-scale activated sludge systems are being used to evaluate the fates of the waste constituents in an aerobic system.

DECONTAMINATION OF BUILDINGS, EQUIPMENT AND DEBRIS AT SUPERFUND SITES

by: Michael L. Taylor, Majid A. Dosani, John A. Wentz, Roxanne B. Sukol, William R. Parker, and Jack S. Greber, PEI Associates, Inc., Cincinnati, Ohio.

Naomi P. Barkley, EPA Hazardous Wastes Engineering Research Laboratory (HWERL), Cincinnati, Ohio.

John Woodyard, IT Corporation, Knoxville, Tennessee.

Pat Esposito, BHE, Inc., Cincinnati, Ohio

ABSTRACT

It is well known that a large number (>1000) of sites in the United States are contaminated with hazardous chemical residues. Many of these hazardous waste sites include structures (houses, office buildings, manufacturing facilities) which are contaminated with hazardous organic chemicals such as PCBs. In addition, many hazardous waste sites are littered with debris (e.g., scrap metal, masonry materials, pieces of wood, equipment or furniture) which is also contaminated.

Implementation of effective, non-destructive methods for on-site decontamination of structures and debris would reduce the distribution of contamination to off-site locations and could facilitate reoccupation of the contaminated site including the structure. Several methods for decontaminating structures are available and have been implemented as described in the "Guide for Decontaminating Buildings, Structures and Equipment at Superfund Sites" (EPA 600/2-85/028); however at this time data are not available which provide reliable indications of the relative efficiencies of these various decontamination procedures.

The goal of this project is to generate reliable data which are indicative of the relative efficiencies of various debris and building decontamination methods. Principle tasks include: 1) location of actual structures contaminated with hazardous wastes which afford suitable sites for comparative evaluations of building and debris decontamination procedures, and 2) performance evaluations of promising building and debris decontamination technologies at the selected field locations.

The first task of this project has now been completed. Several hazardous waste sites were visited and ultimately two PCB-contaminated facilities

were selected which met the established criteria for acceptability. Both facilities are located in Detroit, Michigan and are less than one-half mile apart. A concrete floor of a building located at one of these sites contains levels of PCBs ranging up to 10,000 μg/g, while the second site contains metal and masonry debris which is contaminated with PCBs.

In the second task, which is currently underway, efforts are being focused on evaluation of two emerging technologies for removing PCBs embedded in concrete structures. These two technologies are: 1) A method for in situ degradation of PCB's entailing application of an alkali metal/polyethylene glycolate mixture directly to the concrete surface, and 2) A hydroblasting technique which entails use of a high pressure water jet (30,000 psi) to cut away concrete surfaces. In order to evaluate these PCB removal techniques, concentrations of PCBs in the top one-half inch of the contaminated concrete floor will be determined prior to treatment by analyzing cores obtained from selected locations on the concrete floor. Subsequent to the implementation of each of the decontamination technologies, cores of the treated concrete will again be obtained and the post-treatment PCB concentrations will be assessed. The efficacy of the two decontamination techniques will be judged on the basis of the percent reduction of PCBs achieved with each technique. In addition, the costs of large-scale implementation of each of the two techniques will be calculated and compared.

In addition to the evaluation of concrete decontamination procedures described above, an innovative approach for decontaminating debris will also be evaluated. A prototype of a portable module for on-site decontamination of debris will be designed, built, and tested. The module will consist of an enclosure into which debris can be placed and subsequently solvent-cleaned using a closed loop solvent delivery system. During testing of the prototype, the efficacy of various solvent/additives combinations for removing PCBs from debris will be evaluated.

In this presentation, the status of the work in progress will be thoroughly reviewed.

CHARACTERIZATION OF 2,4,5-T DEGRADATIVE GENES IN PSEUDOMONAS CEPACIA STRAIN AC1100 AND SPONTANEOUS MUTANTS

by: R. A. Haugland
J. Johnson
U.M.X. Sangodkar
A. M. Chakrabarty
University of Illinois at Chicago
Chicago, Illinois 60612

P. R. Sferra
A. Kornel
U. S. Environmental Protection Agency
Cincinnati, Ohio 45268

ABSTRACT

Pseudomonas cepacia strain AC1100 is currently being evaluated in the treatment of aqueous solutions different chlorinated phenoxyacetates and phenols. The introduction of a naturally-occurring plasmid into this organism was shown to extend the range of compounds that it efficiently degrades. Other studies have shown that the ability of AC1100 to degrade 2,4,5-trichlorophenoxyacetic acid (2,4,5-T) and 2,4,5-trichlorophenol is often lost due to instability within certain regions of this organism's genome. Two such regions have been isolated and identified is containing 2,4,5-T degradative genes using molecular cloning and phenotypic complementation procedures. Work is presently in progress to determine the physical basis for the instability of these DNA regions.

DEMONSTRATE COMPUTER ASSISTED ENGINEERING (CAE) TECHNIQUES OR REMEDIAL ACTION ASSESSMENT

P. R. Cluxton, W. G. Harrar, and L. C. Murdoch
University of Cincinnati
Department of Civil & Environmental Engineering
Cincinnati, Ohio 45221

ABSTRACT

A computer workstation dedicated to remedial action assessment is being developed. The system is composed of several off-the-shelf software and hardware modules, with software development limited to the integration of these modules. The completed system will be an example of a Computer Assisted Engineering (CAE) type system.

The purpose of the project is to demonstrate how the remedial action evaluation process can be improved and expedited thru use of the CAE system. The CAE system capabilities are being demonstrated in two ways. First, several small projects have been undertaken for the regional offices which make use of a limited part of the CAE system, e.g., the contaminant mapping capabilities of the system. Second, a Superfund site is the object of a complete demonstration of the CAE system capabilities.

ACTIVITIES OF THE LOUISIANA STATE UNIVERSITY HAZARDOUS WASTE RESEARCH CENTER

Danny D. Reible
Department of Chemical Engineering
Louisiana State University
Baton Rouge, LA 70803

ABSTRACT

The Hazardous Waste Research Center at Louisiana State University (LSU) is conducting fundamental and exploratory research in these general areas: environmental media/waste interaction, incineration, and alternative methods of treatment/destruction. Individual research projects are being conducted by multidisciplinary groups representing a number of academic departments. One such project currently underway is entitled "Modeling Transport of Multiphase Subsurface Contaminants", and deals with the transport and fate processes of a nonaqueous liquid phase.

The presence of a separated non-aqueous liquid phase in the subsurface often controls the rate and magnitude of ground-water contamination. In addition, remediation efforts that do not directly address the non-aqueous phase material are unlikely to provide cost effective or timely solutions to the ground-water contamination risk. Recent research defining the transport and fate processes of a non-aqueous liquid phase is described in this poster. Process modeling efforts that hold promise of providing practical guidance for regulatory development and site assessment and remediation planning are also described. To-date, a model to predict unsaturated zone infiltration of non-aqueous phases has been developed and preliminary models of saturated zone aquifer/contaminant interactions have been proposed. Equilibrium and mass transfer models between the separate fluid phases and the soil matrix have also been proposed. Preliminary experiments testing modeling ideas for both unsaturated and saturated flow have been completed. Additional validating experiments are underway as well as comparisons to field data. The results attained in each of these areas will be described in the presentation.

INNOVATIVE DELIVERY AND RECOVERY SYSTEMS: HYDRAULIC FRACTURING

Larry Murdoch
University of Cincinnati
Department of Civil and Environmental Engineering
Cincinnati, Ohio 45221

ABSTRACT

A hydraulic fracture will form adjacent to a borehole when injection pressures exceed the sum of the confining stress and the resistance to fracture propagation. Once the fracture is formed, sand is pumped in to hold it open and provide a high permeability channelway that can be used to increase both the recovery of contaminants and the delivery of remediating substances.

Preliminary investigations, which consist of theoretical calculations and analogies to applications reported by the energy industry, suggest that hydraulic fractures can be created in many sites of contamination. The orientation of the fractures is expected to be either horizontal in rock and over-consolidated soil, or vertical in normally consolidated soil. Lengths of hydraulic fractures are expected to be similar to their depths of origin, and widths are expected to range from several mm to several cm. Some horizontal fractures lift their overburden and they could be one or more dm in thickness.

Possible application of hydraulic fracturing include increasing the efficiency of pump and treat systems, stimulating the extraction of vapor phases from tight soils, or forming a horizontal sheet-like drain to capture the permeant in a leaching operation.

Currently, we are conducting lab experiments to measure the fracture toughness--or resistance to fracture--of soils as a function of water content or composition. Field experiments into the mechanics of hydraulic fracturing in glacial till are planned for early spring 1988. Preliminary results will be available at the Symposium.

INCINERATION OF NITRATED PESTICIDES IN A LOW NOx PRECOMBUSTOR/PACKAGE BOILER SIMULATOR

William P. Linak, Joseph A. McSorley
Combustion Research Branch, MD-65
Air and Energy Engineering Research Laboratory
U.S. Environmental Protection Agency
Research Triangle Park, NC 27711

Ravi K. Srivastava, Jeffrey V. Ryan
Acurex Corporation
4915 Prospectus Dr.
Research Triangle Park, NC 27713

ABSTRACT

An investigation examining the incineration characteristics of the nitrated pesticide, dinoseb (2-sec-butyl-4,6 dinitrophenol), was conducted by EPA's Office of Research and Development/Air and Energy Engineering Research Laboratory (ORD/AEERL) and Acurex personnel on EPA's 879 kW (3,000,000 Btu/hr) low NOx precombustor/package boiler simulator. The purpose of this study was to provide EPA's Office of Pesticides and Toxic Substances (OPTS) with technical information regarding incineration disposal options if these types of pesticides are banned from further use. Specific information desired included the destruction and removal efficiencies (DREs), and measurement of nitrogen oxide (NOx) emissions under different incineration conditions, some of which included combustion strategies for NOx control. Additionally, qualitative measurement of products of incomplete combustion (PICs), and quantitative particulate emissions were sought. In conjunction with the Hazardous Waste Engineering Research Laboratory (HWERL), the AEERL study examined a class of dinoseb product consisting of dinoseb in organic solvent. Future tests are intended to examine a second class of dinoseb in alcohol, alkanolamine, and water.

Results to date indicate that, although spiked dinoseb blank recovery from XAD-2 resin was low (approximately 10 percent), no dinoseb was detected in any incineration sample taken by modified glass SASS technique and analyzed by GC/MS. Based on instrument sensitivity and dinoseb recovery, DREs greater than 99.99 percent were achieved. PIC emissions, measured by SASS and VOST sampling in conjunction with GC/MS analysis, indicate several common combustion PICs in concentrations typically less than 10 ppb. Particulate emissions were below the RCRA limit of 180 mg/sm3, and consisted primarily of calcium sulfate and calcium oxide. Nitric oxide (NO) emissions without any form of combustion modification for NOx control exceeded 4400 ppm (corrected to 0 % oxygen). When NOx controls, in the forms of air staging and natural gas reburning, were employed these emissions were reduced to below 150 ppm. Dinoseb contains 11.76 percent nitrogen.

ASSESSMENT OF INTERNATIONAL TECHNOLOGIES FOR SUPERFUND APPLICATIONS

Thomas J. Nunno
Jennifer A. Hyman
Alliance Technologies Corp.
Bedford, MA

ABSTRACT

Site remediation is a pressing issue in European countries due to limited availability of land. As a result, much progress is being made in the development of effective technologies for remediating contaminated sites. The purpose of this program was to investigate successful and innovative foreign technologies for potential application to the United States market. This EPA-sponsored project was based on a 6-month research effort which identified 95 innovative technologies in use or being researched worldwide. The most promising technologies from this group were studied in-depth through personal interviews with the scientists who research and apply these technologies and through tours of laboratory models and full-scale installations. These technologies, developed in Holland, West Germany, and Belgium, include vacuum extraction of hydrocarbons from soil, in situ washing of cadmium-polluted soil, rotating biological contactors for treating pesticides in ground water, high-temperature slagging incineration of low-level radioactive wastes, in situ steam stripping, and a number of composting and soil washing operations. The results of this program provide a detailed description of 12 site remediation techniques that have shown promise in lab studies or in full-scale practice.

PREDICTION OF THE FATE OF TOXIC METALS IN HAZARDOUS WASTE INCINERATORS

by: R.G. Barton, P.M. Maly, W.D. Clark, and W.R. Seeker
Energy and Environmental Research Corporation
Irvine, California 92718

C.C. Lee
Hazardous Waste Engineering Research Laboratory
U.S. Environmental Protection Agency
Cincinnati, Ohio

ABSTRACT

Emission of toxic metals during the incineration of metal bearing wastes presents a potential health hazard of increasing interest to federal and state regulatory agencies. A model which predicts the emission of metals from combustion devices is being developed to aid in the formulation of effective regulations and control strategies. Before such a model could be developed, it was necessary to identify the phenomena that control the behavior of metals during the incineration of waste materials. Examination of the characteristics of emissions from a wide variety of incinerators led to the identification of the following potentially important phenomena:

- Reactor thermal behavior
- Particle entrainment
- Metals reactions
- Metals vaporization
- Vapor condensation
- Particle coagulation
- Particle removal by air cleaning equipment.

Submodels addressing each of these phenomena were adapted from existing models or were developed as new models. These submodels were assembled into a composite model for metals partitioning in hazardous waste incineration.

The model was used to assess the impacts of various parameters on metal emissions. Parameters considered include:

- Combustor temperature
- Waste chlorine content
- Saturation ratio
- Entrained particle size distribution
- Gas residence time

- Waste sulfur content
- Gas oxygen concentration
- Metal

Temperature of the burning waste, waste chlorine content, gas oxygen concentration and the metals present were found to have the strongest effects on the predicted emissions.

Data which can be used to verify the model is scarce. However, comparisons of the model's predictions with the experimental data which is available indicate that the model correctly accounts for key phenomena.

LOADING POINT PUNCTURABILITY ANALYSIS OF GEOSYNTHETIC LINER MATERIALS

by: Daren L. Laine
Michael P. Miklas, Jr.
Charles H. Parr
Southwest Research Institute
San Antonio, Texas 78284

ABSTRACT

This study examined geomembrane liner performance in laboratory tests designed to subject several different liner materials to varying pressures, temperatures, and point loads. Point loads were induced by placing the geomembrane material over truncated rigid epoxy cones arranged in three-cone clusters in a sand subgrade and applying a hydrostatic load to the top side of the liner. Cone heights of 9.5, 19.0, and 25.4 millimeters (mm) above the subgrade were used in this study. Preliminary tests resulted in the selection of a cast epoxy resin cone having a 35-degree apex angle and truncated 2.8 mm from the apex at 45 degrees to the cone axis. Polyvinyl chloride (PVC), chlorosulfonated polyethylene (CSPE), and high density polyethylene (HDPE) materials, in two thicknesses each, were subjected to a constant hydrostatic load of 17.93 kilovoltamperes (kPa) at 23°C and 50°C over a 365-day period. HDPE material measuring 1.5 mm thick failed for the loading point height of 25.4 mm above the subgrade. After 365 days, the loading pressure was increased to 60.03 kPa for an additional 30 days. Failures were induced in 1.5-mm HDPE for loading point heights of 19.0 and 25.4 mm and in 2.5-mm HDPE for loading point heights of 25.4 mm. Nonwoven geotextile fabric material of 1.5, 3.8, and 5.3 mm was placed between the liner and the loading points and selected tests were run. HDPE with a thickness of 1.5 mm failed for a loading point height of 19.0 mm with a 1.5-mm geotextile placed between the HDPE and the loading point. These tests were conducted at 17.94-kPa pressure and ambient temperature. HDPE with a thickness of 2.5 mm overlaying a 3.8-mm geotextile failed under 60.03-kPa pressure for a 25.4-mm loading height at the high temperature test condition. No materials failed when overlaid upon a 5.3-mm geotextile for any of the test temperatures or loading heights. Transient pressure loading tests of the membrane material without geotextile support showed failures when the pressure rate of change exceeded 55.20 kPa per hour. The maximum pressure load on the membrane proved to be the failure stress factor rather than the rate at which pressure was applied.

The test results indicate that moderate economic benefit may be gained by allowing larger particles than current engineering practice deems acceptable to remain in a subgrade surface. The loading point heights at which the respective materials failed are correlated with the related subgrade construction and geosynthetic material costs. With PVC and CSPE, without a geotextile underlay, particles as large as 25.4 mm above the subgrade would not be expected to cause liner failure under conditions analogous to the study parameters. Finished installation cost savings of up to 28 percent might result if the largest particles in the subgrade were comparable with the tested sizes. Performance of all of the liner materials was improved with the addition of geotextiles, indicating a positive cost-benefit advantage when a geotextile underlay is used with a geomembrane liner.

RESULTS OF A LABORATORY CHARACTERIZATION OF PULP AND PAPER MILL SLUDGE AND FLY ASH OF POTENTIAL UTILIZATION AS HYDRAULIC BARRIER CONSTRUCTION MATERIAL IN LANDFILLS

by: Van Maltby
Jay P. Unwin
National Council of the Paper Industry
for Air and Stream Improvement, Inc.
Kalamazoo, Michigan 49008-3844

ABSTRACT

A laboratory investigation of the physical characterization of sludge and fly ash produced by the pulp and paper industry was conducted. Sludge samples were collected from both primary and secondary wastewater treatment operations, and fly ash samples were collected from wood, coal, and wood/coal fired boilers. Hydraulic conductivity was the chief parameter of interest. Special procedures were developed for the design and operation of both rigid-wall and flexible-wall permeameters due to the potential for biological activity and the low strength/high compressibility nature of sludges. To minimize the effects of consolidation, permeameters were operated at very low hydraulic gradients (4 to 6). Hydraulic systems were converted from falling-head to constant-head to minimize variations in stress caused by a variable head. Back pressure was utilized in both types of permeameters to ensure a greater degree of saturation.

Results suggest that there are a variety of industry wastes that are sufficiently impermeable to serve as barrier materials in landfill covers (having hydraulic conductivities of 10^{-6} to 10^{-7} cm/sec or less). Fifteen sludges tested had hydraulic conductivities ranging from 10^{-5} to 10^{-8} cm/sec, which generally decreased with time. Eight fly ashes tested had hydraulic conductivities between 10^{-3} and 10^{-7} cm/sec.

THE U.S. EPA COMBUSTION RESEARCH FACILITY

by: Larry R. Waterland, Robert W. Ross, and Johannes W. Lee
Acurex Corporation
Jefferson, Arkansas 72079

ABSTRACT

During FY'87, 25 weeks of incineration testing took place in which 53 individual incineration tests were completed under the operations and research program at the EPA Combustion Research Facility in Jefferson, Arkansas. Test programs completed included: an extended evaluation of the fate of volatile trace metals fed to the liquid injection incineration system (LIS) and testing to evaluate the valence state of chromium discharges from the LIS; testing to support evaluation of the composition of residual discharges from the incineration of five listed hazardous wastes from specific sources; and preliminary evaluation testing of the American Combustion Pyretron Thermal Destruction System as an innovative Superfund site waste treatment technology. Results from these tests are abstracted in this poster. Detailed results from the American Combustion Pyretron system tests are discussed in a separate paper in this symposium.

WASTE REDUCTION INNOVATIVE TECHNOLOGY EVALUATIONS (WRITE) PROGRAM

by: Michael F. Szabo
PEI Associates, Inc.
Cincinnati, OH

Harry M. Freeman
HWERL, U.S. EPA
Cincinnati, OH

ABSTRACT

The purpose of this poster session will be to familiarize conference participants with the WRITE program that HWERL is initiating as a part of its Waste Minimization Research Program. The WRITE program is designed to involve EPA with private industry to encourage the development and/or demonstration of effective techniques and technology for hazardous waste minimization. Initial plans are to structure the program with private industry to be similar to the Agency's Superfund Innovative Technology Evaluation (SITE) program where EPA generally provides funds to support only the evaluation of the demonstration. The WRITE program will therefore provide credible technical information on new waste minimization processes. This paper will provide background on the WRITE program and discuss program activities planned for FY88 and 89.

CASE HISTORIES OF UNDERGROUND STORAGE TANK CORRECTIVE ACTIONS

by: Joyce K. Hargrove and William M. Kaschak
CDM Federal Programs Corporation
Fairfax, Virginia

Robert W. Hillger and Richard A. Griffiths
U.S. Environmental Protection Agency
Hazardous Waste Engineering Research Laboratory
Edison, New Jersey

ABSTRACT

The Environmental Protection Agency's (EPA) proposed regulations for underground storage tanks (UST) require that corrective action be taken in response to leaking UST. However, the experience of personnel in the EPA regions, the states, and the local environmental agencies in this new field varies widely. As a result, what constitutes appropriate corrective action for leaking underground storage tanks is not well defined. The EPA is expanding its Case History File (File) database to facilitate technology transfer among the new personnel involved in underground storage tank corrective actions and those involved in hazardous waste site cleanup.

The File contains reports submitted by On-Scene Coordinators (OSCs) and Remedial Project Managers (RPMs) about technical, administrative, financial, political, and other aspects of the spill and waste-site cleanups they have handled. The File consists of a database section, which allows computerized searches to be made, and a narrative section, which is a detailed report on the response. The database section offers menu-controlled searches in any of 27 categories. The narrative section is organized into the following 10 subsections: General Information, Chemical Information, Effects of the Incident, Site Characteristics, Containment Actions, Removal/Cleanup Actions, Treatment Actions, Disposal Actions, Operational Considerations, and Termination of the Response. The File is being modified to incorporate additional data relevant to UST, such as methods of detection, causes of the leak, tank/piping construction, etc. New reports are being added as the EPA receives them from the states and regions.

The File may be accessed with the use of a computer with modem; a telecommunications program; and a user's guide which provides detailed instruction on the system's operation. The File is managed by the Technical Information Exchange (TIX), Releases Control Branch of the EPA's Hazardous Waste Engineering Research Laboratory in Edison, New Jersey.

This poster describes the Case History File and presents synopses of underground storage tank case histories.

HOSPITAL WASTE INCINERATION

by: Teri L. Shearer
U. S. Environmental Protection Agency
Cincinnati, OH 45268

ABSTRACT

The popularity of infectious waste incineration has grown steadily since the 1984 amendments to the Resource Conservation and Recovery Act of 1976 were passed; these amendments banned the landfill of such untreated wastes. Generators of hospital waste are now responsible for treating and disposing of an estimated 5,900 tons of waste/day, of which a significant portion consists of plastics, pathogens and RCRA regulated components. Emissions range from particulates and PCBs to potentially viable viruses.

Currently there are no federal regulations in force that mandate the control of emissions from hospital waste incinerators. Until clear-cut data is presented that corroborates harmful health and environmental effects, the need for such regulations will, in all likelihood, remain unwarranted. The majority of states have non-specific requirements for the disposal of hospital wastes. However, most are complicated and rarely address the key issue of emission control (although this aspect is changing due to increased public awareness and concern). Combined with the innate incapability of some existing hospital waste incinerators to adequately handle the complex waste streams, it is apparent that the need for concerted effort to investigate, rectify and regulate hospital waste incinerators now exists.

ASSESSMENT OF SOLIDIFICATION/STABILIZATION TECHNOLOGIES FOR SUPERFUND CONTAMINATED SOILS

Richard M. McCandless, P.E., C.P.G.
Department of Civil & Environmental Engineering
University of Cincinnati
Cincinnati, Ohio 45221

ABSTRACT

Solidification/Stabilization treatment processes are currently being evaluated as possible cost effective alternatives for high volume, low contaminant concentration soils at Superfund sites. Work is now in progress at the Center Hill Solid and Hazardous Waste Research Facility (HWERL, Cincinnati) to assess the feasibility and efficacy of various solidification/stabilization technologies. General objectives of this program are to:

- determine technical justification for current standard test methods used to evaluate process performance and recommend modifications or new methods as appropriate;
- provide technical assistance services to the EPA Regions in the form of field and/or laboratory treatability studies; and
- contribute to the development of a broad technical data base characterizing the performance of various treatment processes applied to a range of soil/contaminant systems.

Since initiation of the project in October 1986, a capability to perform most of the standard physical and leaching test procedures has been established. Service activities to date have included field and laboratory studies to evaluate the performance of generic or vendor-proposed solidification/stabilization processes for use at the United Chrome, Sand Springs and Whitehouse Oil Pits NPL sites. Current research tasks include the testing of standard analytical reference matrix (SARM) soils in support of Agency efforts to establish BDAT performance levels and the testing of modified SARM soils to more fully evaluate various leaching test methods currently considered to be the primary measures of performance.

SMALL QUANTITY GENERATOR RESEARCH PROGRAM: MINNESOTA TECHNICAL ASSISTANCE PROGRAM

by: Cindy A. McComas
Minnesota Technical Assistance Program
University of Minnesota
Minneapolis, MN 55455

James Bridges
U.S. EPA
Cincinnati, OH

ABSTRACT

The U.S. Environmental Protection Agency (EPA) has established a Small Quantity Generator Research Program with the special hazardous waste needs of small businesses in mind. This program is developing and promoting the use of innovative technologies and management practices that reduce or prevent the generation of hazardous waste, through a number of research, development, and demonstration projects. Results of this program are providing practical and economical solutions to assist small businesses with proper hazardous waste management, reduction, and regulatory compliance, in a non-regulatory framework. In order to achieve the objectives of this program, a two-year cooperative agreement was established between the EPA and the Minnesota Technical Assistance Program (MnTAP). This cooperative agreement established a small quantity generator research awards program in Minnesota. The research program is designed to provide small quantity generators of hazardous waste with new methods or technologies for waste reduction, or new applications of existing technologies. A total of nine research awards have been established with industry, associations, and academic institutions in Minnesota. Topic areas for these research awards include cyanide detoxification using ozonation and blue-green algae, pesticide rinsate reuse and recycle, treatment of chromic acid laboratory waste, optimizing the use and reuse of water-soluble coolant, organic solvent removal from wastewater using photooxidation, metal removal and recovery from radiator repair wastewaters, copper and lead recovery from metal finishing wastewaters using aluminum displacement, redesign of chemistry lab experiments to minimize waste, and treatment of caustic degreaser waste from engine rebuilding shops. Results from these projects will be disseminated through publications and presentations to benefit small quantity generators nationwide.

PILOT-SCALE PHYSICAL SEPARATIONS FOR TREATMENT OF ORGANIC HAZARDOUS WASTES

Jeffrey P. Herrin and Sardar Q. Hassan
Department of Civil and Environmental Engineering
University of Cincinnati
Cincinnati, Ohio 45221-49TE

Douglas W. Grosse
Hazardous Waste Engineering Research Laboratory
U.S. Environmental Protection Agency
Cincinnati, Ohio 45268

ABSTRACT

With the increasing demand for elimination and/or reduction of land disposal of hazardous waste, it has become necessary to look for viable alternative waste treatment technologies. As a part of the USEPA "Hazardous Waste Treatment Technologies Assessment" program, various physical separation processes will be tested for treatment of organic hazardous wastes. These processes include steam stripping of volatile organics, batch distillation for solvent recovery, solvent extraction and activated carbon adsorption. Test plans for different technologies are at different stages of development with steam stripping and batch distillation as active projects for current fiscal year and solvent extraction and carbon adsorption as future projects. After thorough review of EPA listed hazardous wastes and existing technologies a number of wastes have been identified as probable test wastes for steam stripping and batch distillation. A steam stripping unit with a two inch column and variable packing height has been fabricated for removal of volatile organics. A batch distillation unit with a six inch column and fifty theoretical plates has been installed for solvent recovery testing. Results of the tests and future plans in this area will be presented.

APPLICATIONS OF SUPERCRITICAL EXTRACTION TO ENVIRONMENTAL CONTROL

by: Gregory W. Leman, Steven R. Alferi, David L. Tomasko & Charles A. Eckert
Department of Chemical Engineering
University of Illinois, Urbana, IL. 61801

ABSTRACT

Preliminary economic analyses have already demonstrated that the extraction of organic toxins by supercritical fluids may have substantial cost advantages over the conventional methods currently being practiced. Specific cases studied were extraction of contaminants from soil, and the supercritical fluid regeneration of granular activated carbons (GAC) used in the cleanup of wastewaters and leachates.

We are now in the process of gathering additional experimental data for the refinement of the preliminary designs. We are taking specific data for the solubility of contaminants in supercritical CO_2, and for CO_2 contaiminated with water. Other studies are aimed at the equilibrium between adsorbed contaminants on GAC and supercritical CO_2. Further we have constructed and begun operating a pilot plant for the regeneration of contaminated GAC and the separation of toxins, and we report on these preliminary results as well.

Finally we are using the new data available with process design, simulation, and cost estimation processes such as ChemCAD. For this package we have modified the thermodynamics part in the supercritical and near-supercritical region to reflect the new experimental results. This has permitted much more precise process calculations and economic feasibility studies. The new designs for both mobile and stationary GAC regeneration units are presented.

Results of a Trial Burn of EPA's Mobile Incineration System

by: Gopal Gupta, Robert Sawyer, James Stumbar
Enviresponse, Inc.
8 Peach Tree Hill Road
Livingston, N.J. 07039

Frank Freestone and Joyce Perdek
U.S. E.P.A.
Hazardous Waste Engineering Research Laboratory
Releases Control Branch (Edison, N.J. 08837)
Cincinnati, Ohio 45268

Minda Ho
Linde Division, Union Carbide Corp.
Old Saw Mill River Road
Tarrytown, NY 10591

ABSTRACT

Under the sponsorship of the Office of Research and Development of the U.S. Environmental Protection Agency (EPA), the Mobile Incineration System (MIS) was designed and constructed to demonstrate the high-temperature incineration of toxic and hazardous wastes. The system consists of a refractory-lined rotary kiln, a secondary combustion chamber (SCC), and an air pollution control system mounted on three heavy-duty semi-trailers. Flue gas and stack gas monitoring equipment is contained in a fourth trailer.

In a series of tests and trial burns conducted between 1982 and 1985, the MIS proved its ability to detoxify PCB-contaminated and other chlorinated organic liquids, as well as dioxin-contaminated liquids and soils. The results of these tests and of the field demonstration, during which the MIS has decontaminated 1,000,000 kg of dioxin-bearing materials, have been reported previously.

A trial burn and a series of supplemental tests were conducted on the MIS from June through September, 1987. This work culminated with the issuance of a RCRA permit for pesticide wastes. The MIS was able to achieve the required destruction and removal efficiencies (DREs) for all principal organic hazardous constituents (POHCs) tested. POHCs consisted of: 1,2,4 trichlorobenzene and polychlorinated biphenyls, in both the liquid and solid wastes; carbon tetrachloride, in the liquid waste; and hexachloroethane, in the solid waste.

Preparatory tests conducted prior to the trial burn showed that high rates of chlorine input increased particulate emissions despite satisfactory acid gas removal. Consequently, the air pollution equipment was modified prior to the trial burn.

Supplementary tests were conducted to check the feasibility of feeding pesticide-contaminated vermiculite and brominated sludges. Vermiculite (0.0648 g/cm^3 bulk density) feedrates up to 365 kg/hr were achieved, and measured particulate emissions were well below regulated limits. The tests of solids containing 30% brominated sludge demonstrated a feedrate of 1820 kg/hr.

☆ U.S. GOVERNMENT PRINTING OFFICE: ~~1989~~ 6 4 8 - 1 6 3 87057